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(54) NOVEL PYRIMIDIN-4-ONE AND PYRIMIDIN-4-THIONE AS FUNGICIDE

PYRIMIDIN-4-ON UND PYRMIDIN-4-THION ALS FUNGICIDE

PYRIMIDIN-4-ONE ET PYRIMIDIN-4-THIONE NOUVELLES, UTILES EN TANT QUE FONGICIDE

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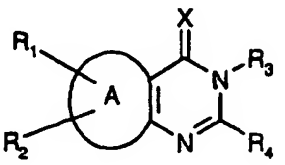
EP 1 015 434 B1

Description

[0001] The present invention relates to novel pyrimidin-4-one and pyrimidin-4-thione derivatives of formula I, which have pesticidal activity, in particular fungicidal activity,



(I)

wherein

A is thienyl, thiazolyl, pyridyl or pyridazinyl;
X is oxygen or sulfur;
R_1 is hydrogen, halogen or trimethylsilyl;
R_2 is hydrogen, halogen or trimethylsilyl; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_8alkyl, C_1-C_8alkenyl, C_1-C_8alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen, C_1-C_6alkoxy or C_1-C_6haloalkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_6alkoxy; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_8alkyl, C_1-C_8alkenyl, C_1-C_8alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen, cyano, C_1-C_6alkoxy or C_1-C_6haloalkoxy; nitro; -CO-C_1-C_6alkyl; C_3-C_6cycloalkyl; or phenyl, which is unsubstituted or mono to tri-substituted by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, cyano, nitro, amino, mono-C_1-C_6alkylamino, di-C_1-C_6alkyl-amino, C_1-C_6alkylthio, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy or C_1-C_6haloalkoxy.

[0002] The invention also relates to the preparation of these compounds, to agrochemical compositions comprising as active ingredient at least one of these compounds, as well as to the use of the active ingredients or compositions for pest control, in particular as fungicides, in agriculture and horticulture.
The compounds I and, optionally, their tautomers may be obtained in the form of their salts. Because the compounds I have at least one basic center they can, for example, form acid addition salts. Said acid addition salts are, for example, formed with mineral acids, typically sulfuric acid, a phosphoric acid or a hydrogen halide, with organic carboxylic acids, typically acetic acid, oxalic acid, malonic acid, maleic acid, fumaric acid or phthalic acid, with hydroxycarboxylic acids, typically ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or with benzoic acid, or with organic sulfonic acids, typically methanesulfonic acid or p-toluenesulfonic acid.
Together with at least one acidic group, the compounds of formula I can also form salts with bases. Suitable salts with bases are, for example, metal salts, typically alkali metal salts or alkaline earth metal salts, e.g. sodium salts, potassium salts or magnesium salts, or salts with ammonia or an organic amine, e.g. morpholine, piperidine, pyrrolidine, a mono-, di- or trialkylamine, typically ethylamine, diethylamine, triethylamine or dimethylpropylamine, or a mono-, di- or trihydroxyalkylamine, typically mono-, di- or triethanolamine. Where appropriate, the formation of corresponding internal salts is also possible. Within the scope of this invention, agrochemical acceptable salts are preferred.

[0003] Where asymmetrical carbon atoms are present in the compounds of formula I, these compounds are in optically active form. Owing to the presence of double bonds, the compounds can be obtained in the [E] and/or [Z] form. Atropisomerism can also occur. The invention relates to the pure isomers, such as enantiomers and diastereomers, as well as to all possible mixtures of isomers, e.g. mixtures of diastereomers, racemates or mixtures of racemates.

[0004] The general terms used hereinabove and hereinbelow have the following meanings, unless otherwise defined:

Alkyl groups on their own or as structural element of other groups such as alkoxy are, in accordance with the number of carbon atoms, straight-chain or branched and will typically be methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-amyl, tert-amyl, 1-hexyl, 3-hexyl, 1-heptyl or 1-octyl.

Alkenyl will be understood as meaning straight-chain or branched alkenyl such as allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, 1-pentenyl, 1-hexenyl, 1-heptenyl or 1-octenyl. Preferred alkenyl radicals contain 3 to 4 carbon atoms in the chain.

Alkynyl can likewise, in accordance with the number of carbon atoms, be straight-chain or branched and is typically propargyl, but-1-yn-1-yl, but-1-yn-3-yl, 1-pentinyl, 1-hexinyl, 1-heptinyl or 1-octinyl. The preferred meaning is propargyl.

Halogen and halo substituents will be understood generally as meaning fluorine, chlorine, bromine or iodine. Fluorine, chlorine or bromine are preferred meanings.

Haloalkyl can contain identical or different halogen atoms, typically fluoromethyl, difluoromethyl, difluorochloromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl, 3,3,3-trifluoropropyl.

Cycloalkyl is, depending on the ring size, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cycooctyl.

[0005] Preferred compounds are those of formula I, wherein
A is thienyl (subgroup A).

[0006] Within the scope of said subgroup A, those compounds of formula I are preferred wherein

R_1 is hydrogen, fluorine, chlorine, bromine or iodine;
R_2 is hydrogen, fluorine, chlorine, bromine or iodine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkyoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4haloalkoxy (subgroup B).

[0007] A special group within the scope of subgroup B is that of the compounds of formula I, wherein

R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_4cycloalkyl, fluorine, chlorine, bromine or C_1-C_4alkoxy; O-C_1-C_6alkyl; O-C_2-C_6alkenyl; O-C_2-C_6alkynyl; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_4cycloalkyl, fuorine, chlorine, bromine or C_1-C_4alkoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine (subgroup C).

[0008] A preferred group within the scope of subgroup C is that of the compounds of the formula I, wherein

A is thienyl[2.3-d],
X is oxygen,
R_1 is hydrogen, chlorine or bromine;
R_2 is hydrogen, chlorine or bromine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_3-C_5alkyl or O-C_1-C_4alkyl;
R_4 is C_2-C_5alkyl or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl or phenoxy and in which the phenoxy is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine (subgroup D1).

[0009] Another preferred group within the scope of subgroup C is that of compounds of the formula I, wherein

A is thienyl[2.3-d],
X is sulfur,
R_1 is hydrogen, chlorine or bromine;
R_2 is hydrogen, chlorine or bromine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_3-C_5alkyl or O-C_1-C_4alkyl;
R_4 is C_2-C_5alkyl or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl or phenoxy and in which the phenoxy is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine (subgroup D2).

[0010] Another preferred group within the scope of subgroup C is that of the compounds of the formula I, wherein

A is thienyl[3.2-d],
X is oxygen,
R_1 is hydrogen, chlorine or bromine;
R_2 is hydrogen, chlorine or bromine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_3-C_5alkyl or O-C_1-C_4alkyl;
R_4 is C_2-C_5alkyl or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl or phenoxy and in which the phenoxy is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine (subgroup E).

[0011] Another preferred group of compounds are those of formula I, wherein
A is pyridyl, (subgroup F).
[0012] Within the scope of said group F, those compounds of formula I are preferred wherein

X is oxygen;
R_1 is hydrogen, fluorine, chlorine, bromine or iodine;
R_2 is hydrogen, fluorine, chlorine, bromine or iodine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4haloalkoxy (subgroup G).

[0013] Other preferred groups of compounds are those of formula I, wherein
A is thiazolyl, (subgroup K).
[0014] Within the scope of said group K, those compounds of formula I are preferred wherein

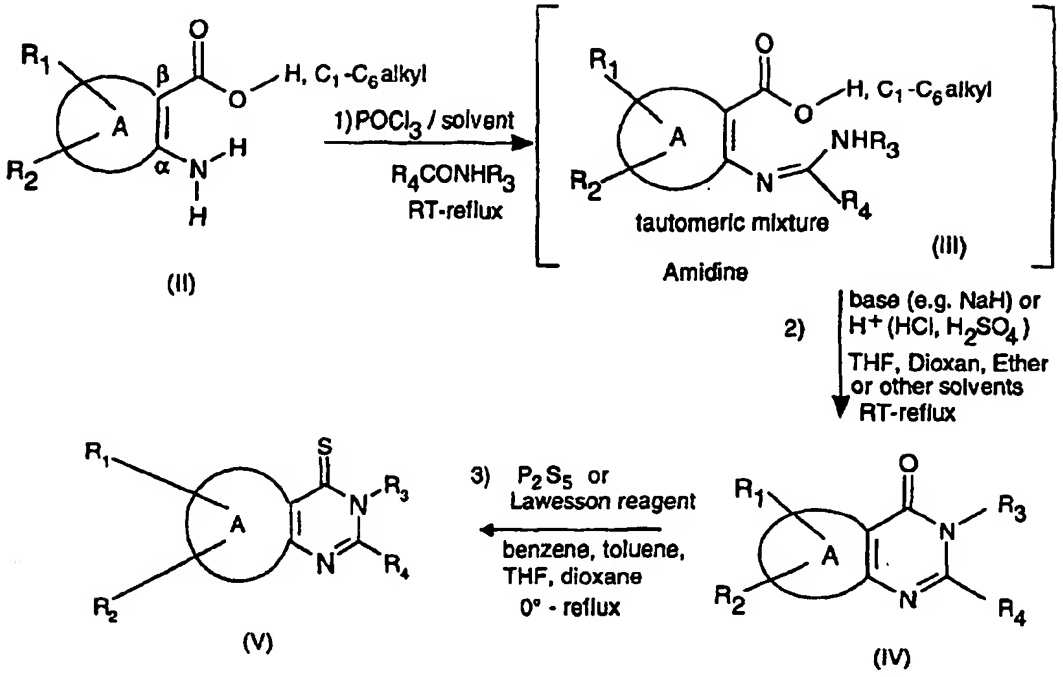
X is oxygen;
R_1 is hydrogen, fluorine, chlorine, bromine or iodine;
R_2 is hydrogen, fluorine, chlorine, bromine or iodine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4haloalkoxy (subgroup L).

[0015] Another preferred group of compounds are those of formula I, wherein
A is pyridazinyl, (subgroup M).
[0016] Within the scope of said group M, those compounds of formula I are preferred wherein

X is oxygen;
R_1 is hydrogen, fluorine, chlorine, bromine or iodine;
R_2 is hydrogen, fluorine, chlorine, bromine or iodine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4haloalkoxy (subgroup N).

[0017] The compounds of formula I can be prepared as follows:

Scheme 1



[0018] The compounds of formula I are preferably prepared starting from α-amino-β-carboalkoxy-heterocycles or α-amino-β-carbocyclic acid heterocycles, some of which, where Het = thienyl, are commercially available (2 isomers). The methyl thiophene-2-amino-3-carboxylate can be prepared, for example, in accordance with Acta Pharm. Suecica 1968, Vol. 5, p.563, according to S.Gronowitz et al. Other heterocycles can be prepared according to instructions in the literature. The synthesis of, for example, ethyl 5-aminothiazole-4-carboxylate and ethyl 5-amino-2-methylthiazole-4-carboxylate is described by Golankiewicz et al. in Tetrahedron 1985, 41, 5989. The reaction of the α-amino-β-carboalkoxyheterocycles or α-amino-β-carbocyclic acid heterocycles with amides (R_4CONHR_3) (step 1 in scheme 1) is conveniently carried out in the presence of $POCl_3$, $SOCl_2$ or SO_2Cl_2, in solvents, such as $ClCH_2CH_2Cl$, $CHCl_3$, CH_2Cl_2, benzene, toluene, hexane, cyclohexane or others in the temperature range from RT to reflux temperature. The resulting amidines (III) either cyclise spontaneously to the pyrimidin-4-ones or were converted into the cyclised products by treatment with bases such as t-Butyl-O-K, NaH, KH, n-BuLi, NaOH, Na_2CO_3 or others in solvents such as THF, dioxane, hexane, toluene, DMSO, DMF, dimethylacetamid or others at temperatures between 20°C and reflux-temperature. The replacement of the 4-one group with sulfur to the 4-thione group (step 3 in scheme 1) is carried out by reaction with P_2S_5 or Lawesson-reagent in tetrahydrofurane, dioxane or toluene as solvent in the temperature range of RT to reflux temperature.

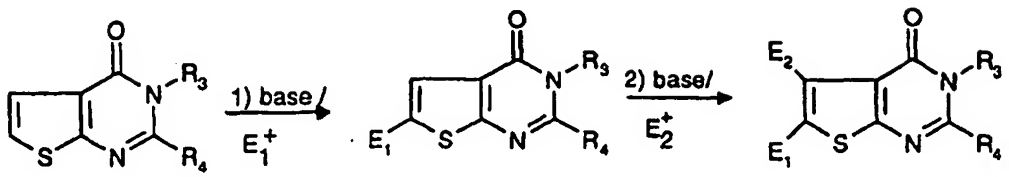
[0019] The above synthesis route is the first disclosure of how to prepare 3H-thieno[2.3-d]-pyrimidin-4-one derivatives within the structural pattern of formula I herein.

[0020] Methods for the preparation of compounds of the general formula I wherein $R_1 = R_2$ = hydrogen are described in Chemical Scripta 1981, 18, 135, Synthesis 1977, 180, Chem.Pharm.Bull. 1989, 37,2122 and DE-OS-2411273.

[0021] The invention also relates to the intermediates of the formula III, IV and V, and especially to those wherein A represents thienyl[2.3-d].

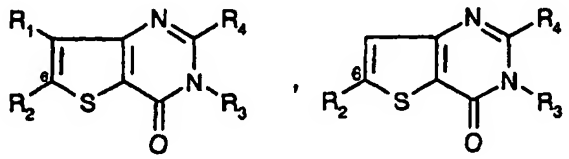
[0022] The introduction of further substituents into the 5-ring of the thienopyrimidin-4-ones may also conveniently be carried out using metallorganic methodology. Thieno[3.2-d]-pyrimidin-4-ones and thieno[2.3-d]pyrimidin-4-ones, for example, can be deprotonised selectively in 6-position. Particularly suitable bases for this purpose are lithium diisopropylamide (LDA), lithium cyclohexylisopropylamide (LICA) or secondary butyl lithium/TMEDA. A great number of the radicals R_1 or R_2 indicated above can be introduced by reacting the resulting anions with electrophiles (step 1 in scheme 2), typically Br_2, NBS, F_2, ICl, Cl_2, F^+ reagents, trimethylsilyl chloride.

Scheme 2 : Synthesis of special heterocycles



$E^+_{1,2}$ = NBS (N-Bromsuccinimide), NCS (N-Chlorsuccinimide), I_2, Cl_2, Br_2, FCl, F^+ reagents, TMS and similar Si reagents.

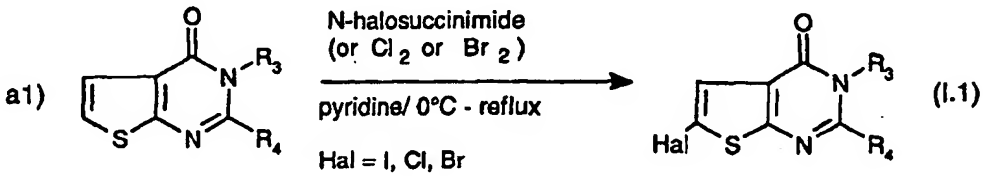
[0023] The following compounds can likewise be prepared in general accordance with the methods described in scheme 2:



Scheme 3 : Synthesis of special thienopyrimidin-4-ones (special methods for the introduction of halogen into the thiophene ring)

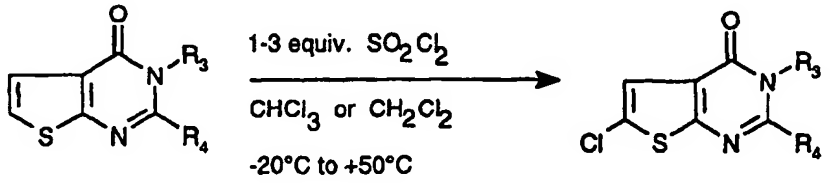
a) Thieno[2.3-d]pyrimidin-4-ones:

[0024]



1-3 molar equivalents of N-bromosuccinimide or N-chlorosuccinimide (or Cl_2 gas or Br_2) are used for halogenation. The solvent used is, for example, pyridine in the temperature range from 0°C to reflux. The reaction time is 1 to 24 hours.

a2) "Pure" chlorinating method :



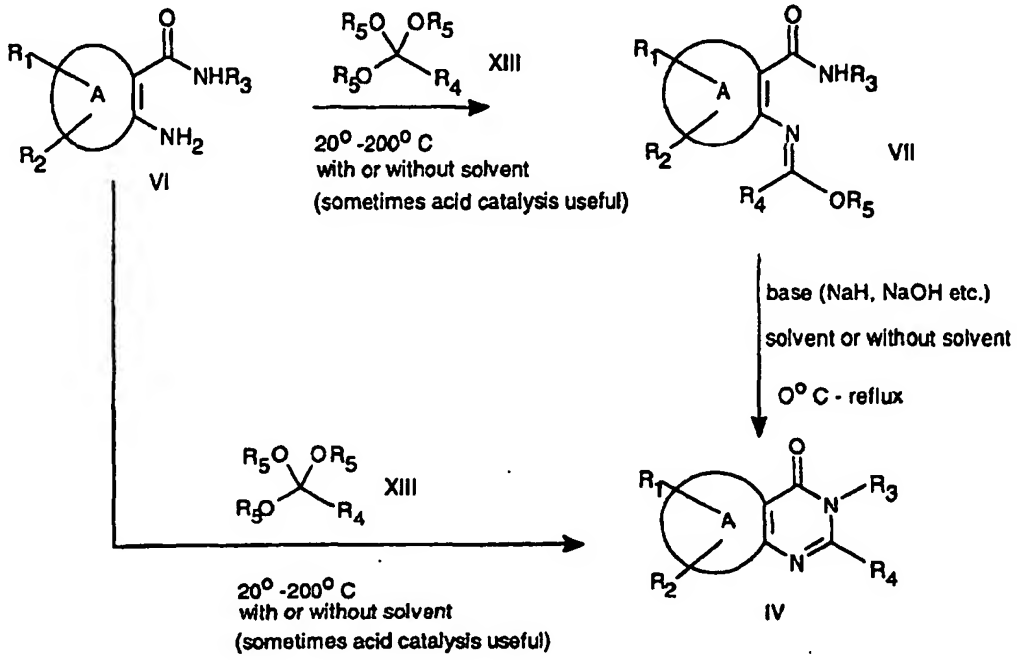
[0025] The described reactions are carried out in per se known manner, e.g. in the presence or absence of a suitable solvent or diluent or of a mixture thereof, if appropriate with cooling, at room temperature or with heating, e.g. in the temperature range from about -20°C to the boiling temperature of the reaction medium, preferably in the range from about -20°C to about +150°C and, if required, in a closed vessel, under pressure, in an inert gas atmosphere and/or under anhydrous conditions.

Illustrative examples of such solvents or diluents are: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, typically benzene, toluene, xylene, chlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, dichloroethane or trichloroethane; ethers, typically diethyl ether, tert-butylmethyl ether, tetrahydrofuran or dioxane; ketones, typically acetone or methyl ethyl ketone; alcohols, typically methanol, ethanol, propanol, butanol, ethylene glycol or glycerol; esters, typically ethyl acetate or butyl acetate; amides, typically N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric acid triamide; nitriles, typically acetonitrile; and sulfoxides, typically dimethylsulfoxide. Bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, can also be used as solvents or diluents.

Suitable bases are, for example, alkali metal hydroxide or alkaline earth metal hydroxide, alkali metal hydride or alkaline earth metal hydride, alkali metal amide or alkaline earth metal amide, alkali metal alkanolate or alkaline earth metal alkanolate, alkali metal carbonate or alkaline earth metal carbonate, alkali metal dialkylamide or alkaline earth metal dialkylamide, or alkali metal alkylsilylamide or alkaline earth metal alkylsilylamide, alkylamines, alkylenediamines, optionally N-alkylated, optionally unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. Examples meriting mention are sodium hydroxide, sodium hydride, sodium amide, sodium methanolate, sodium carbonate, potassium tert-butanolate, potassium carbonate, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, N-methylmorpholine, benzyltrimethylammonium hydroxide, and 1,8-diazabicyclo[5.4.0]undec-5-ene (DBU).

[0026] The compounds of the formula I can also be prepared as follows

Scheme 4:



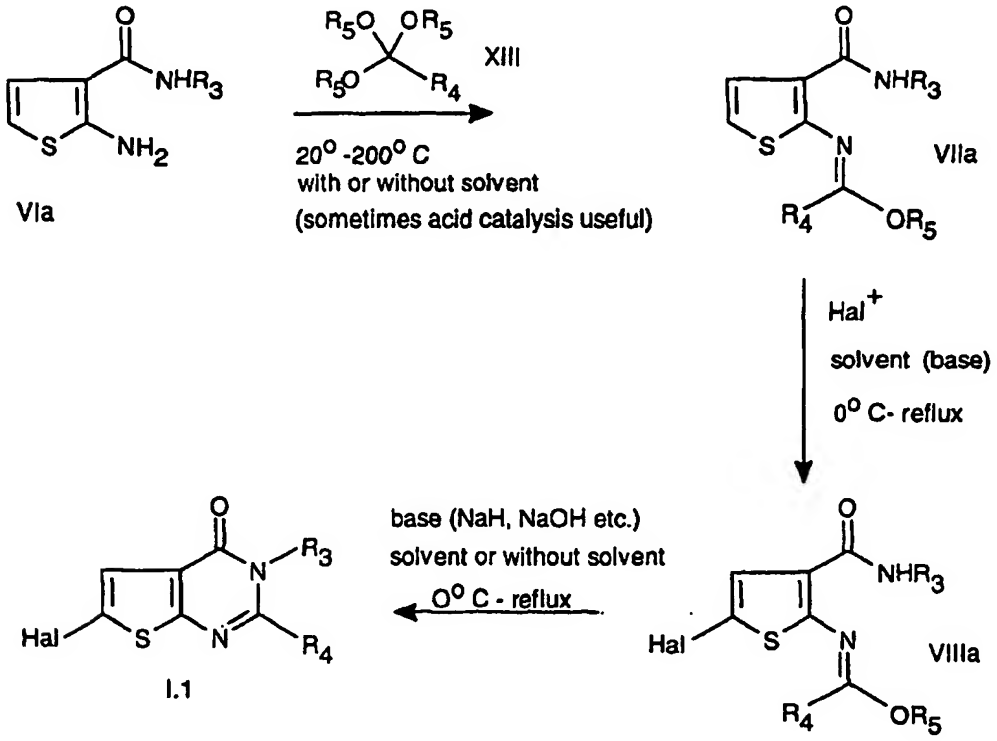
R_5 = C_1-C_6-alkyl

[0027] The amino carboxylic acidamide of formula VI reacts with the orthoester of formula XIII in the presence or absence of a suitable solvent or diluent, if required in the presence of an acid catalyst at room temperature or with heating, e.g. in the temperature range from about 20 to 200°C. Illustrative examples of solvents or diluents are ethers like tert.butylmethylether, tetrahydrofurane, dimethylether; amides like N,N-dimethylformamide or N-methyl-pyrrolidone; sulfoxides, typically dimethylsulfoxid and alcohols like methanol, ethanol, propanol, butanol, ethylene glycol or

glycerol. As catalyst can be used hydrogen halides, methanesulfonic acid, triflouromethyl aceticacid, p-toluenesulfonic acid and others in the absence of water. Commonly used bases are sodium hydroxid, potassium hydroxid, sodium hydrogencarbonate, sodium carbonate, sodium hydride, potassium hydride, potassium carbonate and others.
Especially for the thienopyrimidinone, scheme 5 describes the reaction of the aminothiophene-carboxylic-acid amide VIa with the orthoester XIII in the presence or absence of a solvent, if required in the presence of an acid catalyst in the temperature range from 20 to 200°C. The resulting intermediate VIIa is then halogenated in the presence of a solvent at temperatures from 20°C to reflux. The halogenated intermediate VIIIa is than cyclised in the presence of a base, in the presence or absence of a suitable solvent at temperatures from 20°C to reflux. Halogenation reagents are typically N-Bromsuccinimide, N-Chlorsuccinimide, N-iodsuccinimide, Chlorgas, Br_2, thionylchloride and others. Preferably solvents used for the halogenation are tert-butylmethylether, tetrahydrofurane, chloroform, methylenechloride, pyridine and quinoline.

Scheme 5:

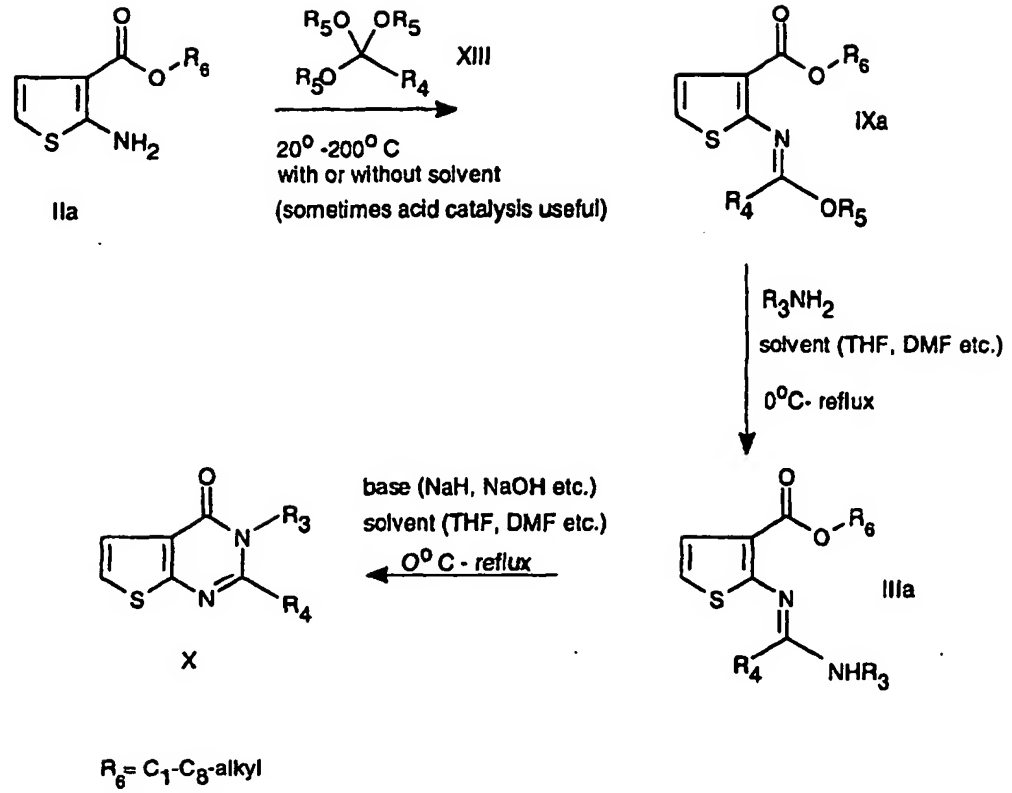
(Thienopyrimidinones)



Hal+ = NCS, NBS, NIS, Cl_2, Br_2, SO_2Cl_2
solvents for halogenation: THF, TBME, $CHCl_3$, CH_2Cl_2, pyridine, quinoline and others

[0028] Another alternative is described in scheme 6, in which the amino-carboalkoxy-thiophene of formula IIa reacts with the orthoester XIII to the intermediate IXa, than the compound IXa is transformed to the amidine IIIa and cyclised to the thienopyrimidinone X. The halogenation of X to obtain I.1 is as described in Scheme 3.

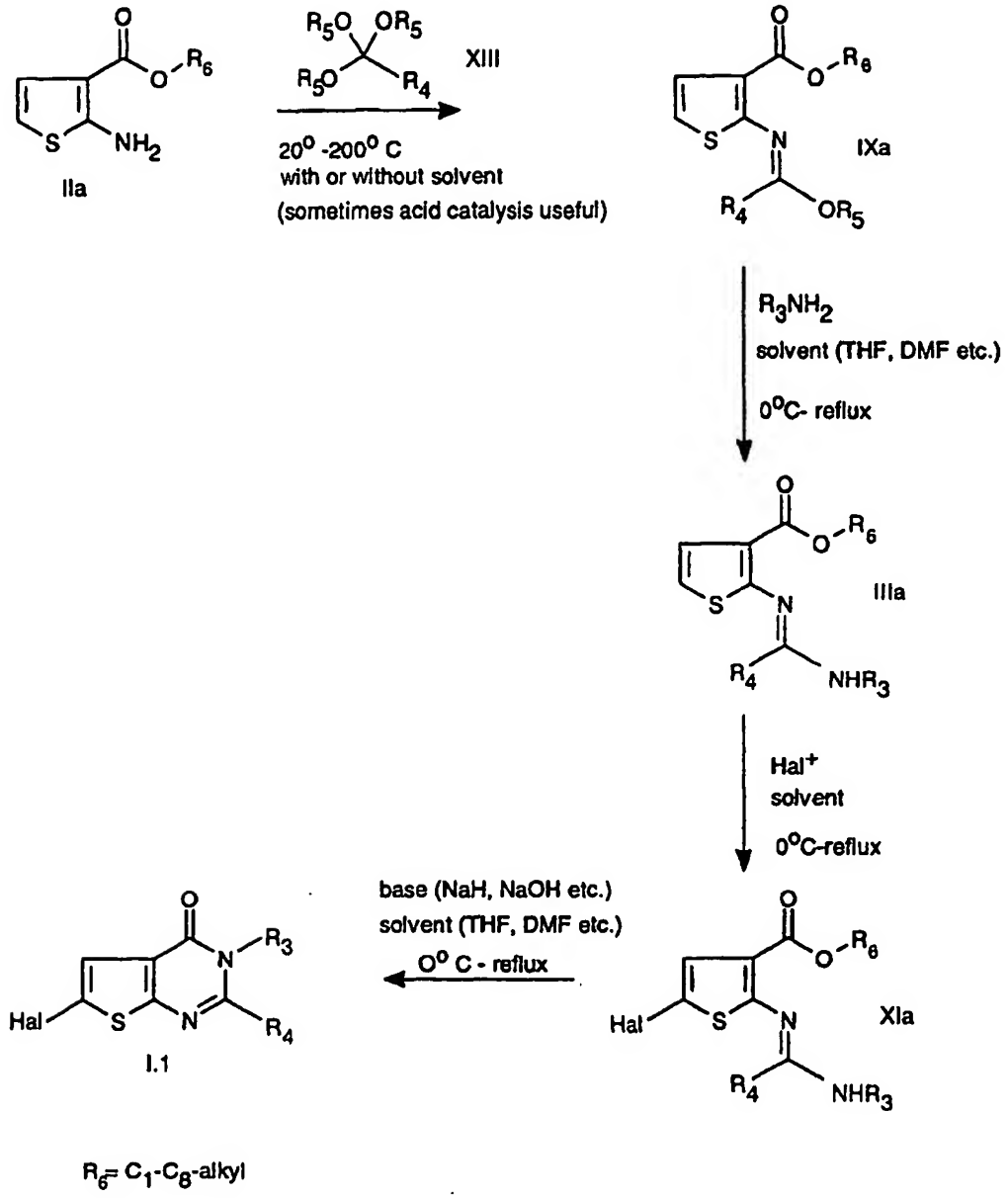
Scheme 6:



[0029] The reaction conditions from IIa to IXa is as described in the schemes 4 or 5, as well as the cyclisation from IIIa to X is as described above. The reaction from IXa to IIIa requires as solvent for example tetrahydrofurane, N,N-dimethylformamide or others at a temperature range from 0°C to reflux.

[0030] The scheme 7 describes the reaction of the compound IIa with the orthoester XIII to obtain the intermediate IXa, which is converted to the intermediate IIIa and than halogenated to the thiophene XIa. Cyclisation of XIa gives the compound I.1.

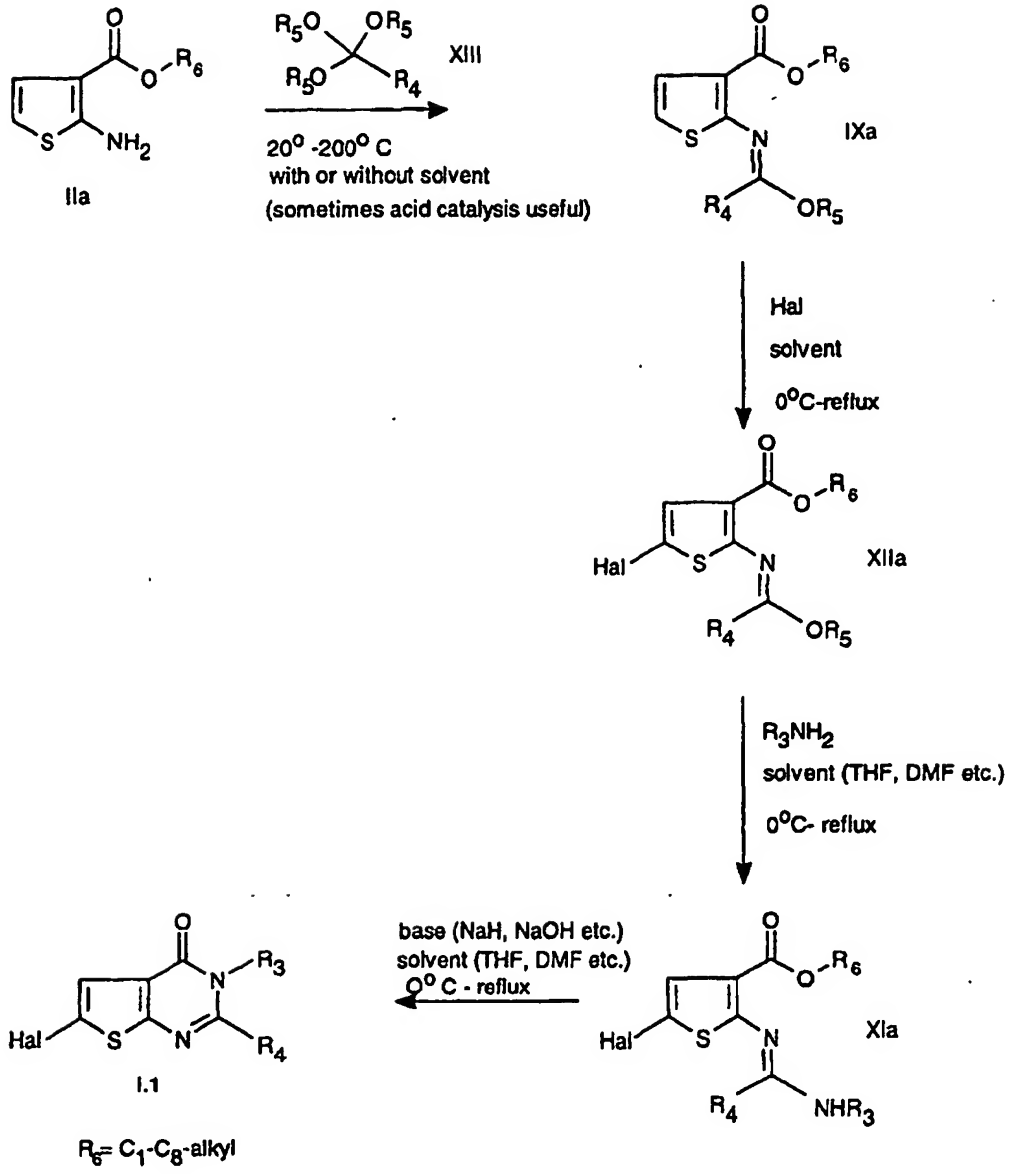
Scheme 7



[0031] The reactions conditions described in process 4 are as described analogously in the schemes 4, 5 or 6.

[0032] Scheme 8 describes the alternative route comprising the reaction of the compound IIa with the orthoester XIII to the intermediate IXa, which is halogenated to the intermediate XIIa and than converted to the thiophene Xla. Cyclisation of Xla gives the end product I.1. The reactions conditions are as described in the schemes 4, 5, 6 and 7.

Scheme 8:



[0033] Quinazolinone derivatives having fungicidal properties are known from WO-94/26722 or EP-A-276825 and thienopyrimidinones are known from WO-97/02262.

[0034] Surprisingly, it has now been found that the novel compounds of formula I have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

[0035] The compounds of formula I can be used in the agricultural sector and related fields as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phy-

topathogenic microorganisms.

[0036] It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

[0037] The compounds I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

[0038] Within the scope of this invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibber plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

[0039] The compounds of formula I are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

[0040] The compounds of formula I can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities.

Mixing components which are particularly preferred are azoles such as azaconazole, bitertanol, propiconazole, difenoconazole, diniconazole, cyproconazole, epoxiconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, tebuconazole, tetraconazole, fenbuconazole, metconazole, myclobutanil, perfurazoate, penconazole, bromuconazole, pyrifenox, prochloraz, triadimefon, triadimenol, triflumizole or triticonazole; pyrimidinyl carbinoles such as ancymidol, fenarimol or nuarimol; 2-amino-pyrimidine such as bupirimate, dimethirimol or ethirimol; morpholines such as dodemorph, fenpropidin, fenpropimorph, spiroxamin or tridemorph; anilinopyrimidines such as cyprodinil, pyrimethanil or mepanipyrim; pyrroles such as fenpiclonil or fludioxonil; phenylamides such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace or oxadixyl; benzimidazoles such as benomyl, carbendazim, debacarb, fuberidazole or thiabendazole; dicarboximides such as chlozolinate, dichlozoline, iprodine, myclozoline, procymidone or vinclozolin; carboxamides such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin or thifluzamide; guanidines such as guazatine, dodine or iminoctadine; strobilurines such as azoxystrobin, kresoximmethyl, metominostrobin, SSF-129 or 2-[α{[(α-methyl-3-trifluoromethyl-benzyl)imino]-oxy}-o-tolyl]-glyoxylic acid-methylester-O-methyloxime; dithiocarbamates such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb or ziram; N-halomethylthio-dicarboximides such as captafol, captan, dichlofluanid, fluoromide, folpet or tolyfluanid; copper compounds such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper or oxine-copper; nitrophenol derivatives such as dinocap or nitrothal-isopropyl; organo phosphorous derivatives such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos or tolclofos-methyl; and other compounds of diverse structures such as acibenzolar-S-methyl, anilazine, blasticidin-S, chinomethionat, chloroneb, chlorothalonil, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, dithianon, etridiazole, famoxadone, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, kasugamycin, methasulfocarb, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine or validamycin.

[0041] Preferred compound for mixing with the above-mentioned mixing components is compound no. 3.30.

[0042] Another preferred compound for mixing with the above-mentioned mixing components is compound no. 3.31.

[0043] Another preferred compound for mixing with the above-mentioned mixing components is compound no. 3.58.

[0044] Another preferred compound for mixing with the above-mentioned mixing components is compound no. 3.59.

[0045] Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers.

A preferred method of applying a compound of formula I, or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk

of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

[0046] The compounds of formula I are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomizing, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

[0047] Advantageous rates of application are normally from 5 g to 2 kg of active ingredient (a.i.) per hectare (ha), preferably from 10 g to 1 kg a.i./ha, most preferably from 20 g to 600 g a.i./ha. When used as seed drenching agent, convenient dosages are from 10 mg to 1 g of active substance per kg of seeds.

[0048] The formulation, i.e. the compositions containing the compound of formula I and, if desired, a solid or liquid adjuvant, are prepared in known manner, typically by intimately mixing and/or grinding the compound with extenders, e.g. solvents, solid carriers and, optionally, surface active compounds (surfactants).

[0049] Suitable carriers and adjuvants may be solid or liquid and correspond to the substances ordinarily employed in formulation technology, such as, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners binding agents or fertilizers. Such carriers are for example described in WO 97/33890.

[0050] Further surfactants customarily employed in the art of formulation are known to the expert or can be found in the relevant literature.

[0051] The agrochemical formulations will usually contain from 0.1 to 99 % by weight, preferably from 0.1 to 95 % by weight, of the compound of formula I, 99.9 to 1 % by weight, preferably 99.8 to 5 % by weight, of a solid or liquid adjuvant, and from 0 to 25 % by weight, preferably from 0.1 to 25 % by weight, of a surfactant.
Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

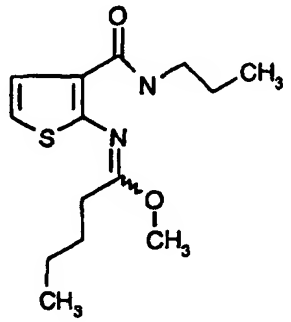
[0052] The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

[0053] The following non-limitative Examples illustrate the above-described invention in more detail. Temperatures are given in degrees Celsius. The following abbreviations are used: Et = ethyl; i-propyl = isopropyl; Me = methyl; m.p. = melting point. "NMR" means nuclear magnetic resonance spectrum. MS = mass spectrum. "%" is percent by weight, unless corresponding concentrations are indicated in other units.

Preparation examples:

Example P-1 : 2-(1-n-butyl-1-methoxymethyleneamino)thiophene-3-carboxylic-acid propylamide

[0054]

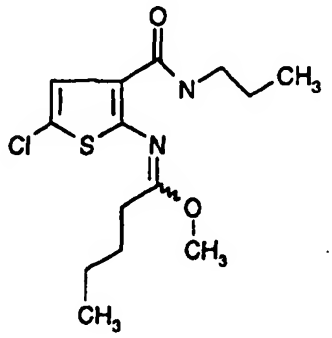


[0055] In a destillation apparatus, a mixture of 1.84 g of 2-aminothiophene-3-carboxylic-acid propylamide and 2.43 g of trimethyl orthovalerate is heated for 2 hours at 130°C. Methanol, which arises during the reaction is directly distilled out of the reaction flask. After cooling, the crude product is purified by column chromatography (eluant: hexane/ethylacetate = 1:2). Yield : 1.9 g pure 2-(1-n-butyl-1-methoxymethyleneamino)thiophene-3-carboxylic-acid propylamide;

m.p. 68-70°C.

Example P-2 : 5-Chloro-2-(1-n-butyl-1-methoxymethyleneamino)thiophene-3-carboxylic-acid propylamide

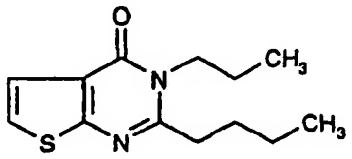
[0056]



[0057] In a sulfonation flask 0.85 g 2-(1-n-butyl-1-methoxymethyleneamino)thiophene-3-carboxylic-acid propylamide are added with stirring to 10 ml absolute pyridine. The internal temperature is then raised to 60°C and 0.5 g of N-chlorosuccinimide (NCS) are added in two portions. After stirring for 1 hour at 60°C, the pyridine is removed in a water jet vacuum. The residue is taken up in ethylacetate and the organic phase is washed twice with water. After drying of the organic phase, the solvent is removed in a water jet vacuum and the raw material purified by column chromatography over silica gel (eluant: hexane/ethylacetate = 3:1). Yield : 0.6 g 5-Chloro-2-(1-n-butyl-1-methoxymethyleneamino)thiophene-3-carboxylic-acid propylamide in the form of brownish crystalls; m.p. 110-112°C.

Example P-3 : 2-n-Butyl-3-n-propyl-3H-thieno[2,3-d]pyrimidin-4-one

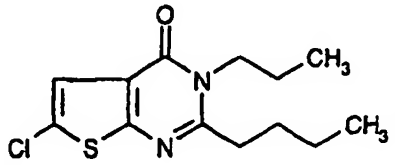
[0058]



[0059] In a sulfonation flask, 0.85 g of 2-(1-n-butyl-1-methoxymethyleneamino)-thiophene-3-carboxylicacid propylamide is dissolved in 20 ml of absolute THF and 0.15 g of a ca. 55% NaH dispersion is added in small portions. The mixture is stirred for 15 minutes at room temperature and 1 hour at reflux temperature. Then the solvent is removed in a water jet vacuum and the residue taken up in ethylacetate. The organic phase is washed twice with water and after drying of the organic phase with sodium sulfate, the solvent is removed in a water jet vacuum. The resulting crude product (yield: 0.8g of 2-n-butyl-3-n-propyl-3H-thieno[2,3-d]-pyrimidine-4-one in the form of a brown liquid) can be used without further purification for the halogenation step.

Example P-4 : 2-n-butyl-6-chloro-3-n-propyl-3H-thieno[2,3-d]pyrimidine-4-one

[0060]

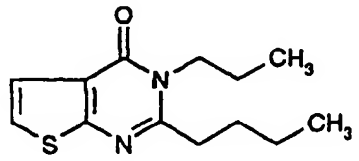


[cmpd. 3.31]

[0061] In a sulfonation flask, 0.36g of 5-Chloro-2-(1-n-butyl-1-methoxymethylene-amino)thiophene-3-carboxylic-acid propylamide is dissolved in 20 ml of absolute THF and 0.085g of a ca. 55% NaH dispersion is added in one portion. The mixture is stirred for 15 minutes at room temperature and 1 hour at reflux temperature. Then the solvent is removed in a water jet vacuum and the residue taken up in ethylacetate. The organic phase is washed twice with water and after drying of the organic phase with sodium sulfate, the solvent is removed in a water jet vacuum. The resulting crude product is purified by column chromatography over silica gel (eluant: hexane/ethylacetate = 5:1). Yield: 0.2 g 2-n-butyl-6-chloro-3-n-propyl-3H-thieno[2,3-d]pyrimidin-4-one in the form of a slightly yellowish powder; m.p. 67-69°C.

Example P-3a : 2-n-butyl-3-n-propyl-3H-thieno[2.3-d]pyrimidin-4-one

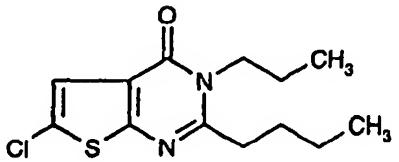
[0062]



[0063] In a sulfonation flask, 11.0 g (70 mmol) of 2-amino-3-carbomethoxythiophen and 10.9 g (76 mmol) valeric acid propylamide are added to 60 ml 1,2-dichloroethane. Under stirring and at room temperature 7 ml of phosphoroxychloride is slowly added dropwise. After 3 hours at reflux temperature the mixture is poored into ice water and adjusted light alkali with sodium hydrogencarbonat. The resulting mixture is then extracted three times with methylenechloride and the separated organic phase dried over sodium sulfate. The solvent is then removed in a water-jet vacuum.
In a sulfonation flask, the crude product is added to 100 ml of absolute tetrahydrofurane and under stirring 4.36 g (0.1 mol) NaH in 50 ml abs. THF is carefully added. After stirring for 2 hours at reflux temperature, the solvent is removed in a water-jet vacuum and the residue is taken up in ethyl acetate/water. The water-phase is extracted with additionally ethyl acetate. The organic phase is dried over sodium sulfate and the solvent removed in a water-jet vacuum. The crude product is purified by column chromatography over silica gel (eluant: TBME/hexane = 1:2). 12.0 g of 2-n-butyl-3-n-propyl-3H-thieno[2.3-d]pyrimidin-4-one are obtained in the form of a yellow powder having a melting point of 70-72°C.

Example P-4a 2-n-butyl-6-chloro-3-n-propyl-3H-thieno-[2.3-d]pyrimidin-4-one

[0064]

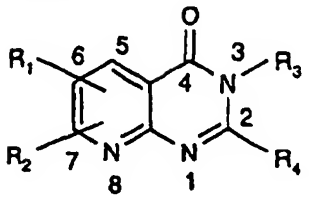


[cmpd. no. 3.31]

[0065] In a sulfonation flask, 2.0 g (8 mmol) of 2-n-butyl-3-propyl-3H-thieno[2.3-d]pyrimidin-4-one are added, with

stirring, to 15 ml of absolute pyridine. The internal temperature is then raised to 80°C and then 1.87 g (14 mmol) of N-chlorosuccinimide (NCS) are added in smallish portions. After stirring for 3 hours at 90°C 1.0 g of NCS is added and the mixture is stirred another 3 hours at 90°C. The pyridine is removed in a water-jet vacuum and the crude product so obtained is purified by column chromatography over silica gel (eluant: n-hexane/tert.butylmethylether = 3:1), giving 0.9 g of 2-n-butyl-6-chloro-3-propyl-3H-thieno-[2.3-d]pyrimidin-4-one in the form of a beige powder having a melting point of 67-69°C.

Tabelle 2: A = Pyridyl



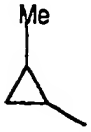
cmpd. No.	R_1	R_2	R_3	R_4	phys. data m.p.°C
2.1	6-Br	H	Me	Me	
2.2	6-Cl	H	Me	Et	
2.3	6-Br	H	Me	n-Propyl	
2.4	6-Cl	H	Me	n-Propyl	
2.5	6-Br	H	Me	n-Butyl	
2.6	6-Cl	H	Me	n-Butyl	
2.7	6-Br	H	Me	i-Butyl	
2.8	6-Cl	H	Me	i-Butyl	
2.9	6-Br	H	Me	n-Pentyl	
2.10	6-Br	H	Me		
2.11	6-Cl	H	Me		
2.12	6-Br	H	Et	Me	
2.13	6-Cl	H	Et	Et	
2.14	6-Br	H	Et	n-Propyl	
2.15	6-Cl	H	Et	n-Propyl	
2.16	6-Br	H	Et	n-Butyl	
2.17	6-Cl	H	Et	n-Butyl	
2.18	6-Br	H	Et	i-Butyl	
2.19	6-Cl	H	Et	i-Butyl	
2.20	6-Br	H	Et	n-Pentyl	
2.21	6-Br	H	Et		
2.22	6-Cl	H	Et		
2.23	6-Br	H	n-Propyl	Me	

2.24	6-Cl	H	n-Propyl	Et	
2.25	6-Br	H	n-Propyl	n-Propyl	
2.26	6-Cl	H	n-Propyl	n-Propyl	
2.27	7-I	H	n-Propyl	n-Propyl	
2.28	6-Br	H	n-Propyl		
2.29	6-Cl	H	n-Propyl		
2.30	6-Br	H	n-Propyl	n-Butyl	Oil, ^{1}H-NMR
2.31	6-Cl	H	n-Propyl	n-Butyl	
2.32	6-I	H	n-Propyl	n-Butyl	
2.33	6-Br	H	n-Propyl	i-Butyl	
2.34	6-Cl	H	n-Propyl	i-Butyl	
2.35	6-Br	H	n-Propyl		
2.36	6-Cl	H	n-Propyl		
2.37	6-Br	H	n-Propyl		
2.38	6-Cl	H	n-Propyl		
2.39	6-Br	H	n-Propyl	Cyclobutyl	
2.40	6-Br	H	n-Propyl	n-Pentyl	
2.41	6-Cl	H	n-Propyl	n-Pentyl	
2.42	6-Br	H	n-Propyl	Cyclopentyl	
2.43	6-Br	H	n-Propyl	n-Hexyl	
2.44	6-Br	H	n-Propyl	Cyclohexyl	
2.45	6-Br	H	n-Propyl	Phenyl	
2.46	6-Br	H	n-Propyl	4-Chloro-phenyl	

2.47	6-Cl	H	n-Propyl	4-Chloro-phenyl
2.48	6-Br	H	n-Propyl	4-Phenoxy-phenyl
2.49	6-Br	H	n-Butyl	Me
2.50	6-Cl	H	n-Butyl	Et
2.51	6-Br	H	n-Butyl	n-Propyl
2.52	6-Cl	H	n-Butyl	n-Propyl
2.53	H	7-Cl	n-Butyl	n-Propyl
2.54	H	7-I	n-Butyl	n-Propyl
2.55	6-Br	H	n-Butyl	
2.56	6-Cl	H	n-Butyl	
2.57	H	7-Cl	n-Butyl	
2.58	6-Br	H	n-Butyl	n-Butyl
2.59	6-Cl	H	n-Butyl	n-Butyl
2.60	6-I	H	n-Butyl	n-Butyl
2.61	6-Br	H	n-Butyl	i-Butyl
2.62	6-Cl	H	n-Butyl	i-Butyl
2.63	6-Br	H	n-Butyl	
2.64	6-Cl	H	n-Butyl	
2.65	6-I	H	n-Butyl	
2.66	6-Br	H	n-Butyl	
2.67	6-Cl	H	n-Butyl	

2.68	6-Br	H	n-Butyl	Cyclobutyl
2.69	6-Br	H	n-Butyl	n-Pentyl
2.70	6-Cl	H	n-Butyl	n-Pentyl
2.71	6-Br	H	n-Butyl	Cyclopentyl
2.72	6-Br	H	n-Butyl	n-Hexyl
2.73	6-Br	H	n-Butyl	Cyclohexyl
2.74	6-Br	H	n-Butyl	Phenyl
2.75	6-Br	H	n-Butyl	4-Chloro-phenyl
2.76	6-Cl	H	n-Butyl	4-Chloro-phenyl
2.77	6-Br	H	n-Butyl	4-Phenoxy-phenyl
2.78	6-Br	H	i-Butyl	n-Propyl
2.79	6-Cl	H	i-Butyl	n-Prpyl
2.80	6-Br	H	i-Butyl	n-Butyl
2.81	6-Cl	H	i-Butyl	n-Butyl
2.82	6-Br	H		n-Propyl
2.83	6-Cl	H		n-Propyl
2.84	6-Br	H		n-Propyl
2.85	6-Br	H		n-Butyl
2.86	6-Br	H	n-Pentyl	Me
2.87	6-Cl	H	n-Pentyl	Et
2.88	6-Br	H	n-Pentyl	n-Propyl
2.89	6-Cl	H	n-Pentyl	n-Propyl
2.90	6-Br	H	n-Pentyl	
2.91	6-Cl	H	n-Pentyl	
2.92	6-Br	H	n-Pentyl	n-Butyl

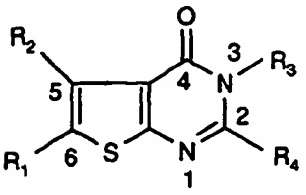
2.93	6-Cl	H	n-Pentyl	n-Butyl
2.94	6-I	H	n-Pentyl	n-Butyl
2.95	6-Br	H	n-Pentyl	i-Butyl
2.96	6-Cl	H	n-Pentyl	i-Butyl
2.97	6-Br	H	n-Pentyl	
2.98	6-Cl	H	n-Pentyl	
2.99	6-Br	H	n-Pentyl	Me 
2.100	6-Cl	H	n-Pentyl	Me 
2.101	6-Br	H	n-Pentyl	Cyclobutyl
2.102	6-Br	H	n-Pentyl	n-Pentyl
2.103	6-Cl	H	n-Pentyl	n-Pentyl
2.104	6-Br	H	n-Pentyl	Cyclopentyl
2.105	6-Br	H	n-Pentyl	n-Hexyl
2.106	6-Br	H	n-Pentyl	Cyclohexyl
2.107	6-Br	H	n-Pentyl	Phenyl
2.108	6-Br	H	n-Pentyl	4-Chloro-phenyl
2.109	6-Cl	H	n-Pentyl	4-Chloro-phenyl
2.110	6-Br	H	n-Pentyl	4-Phenoxy-phenyl
2.111	6-Br	H	Oet	Me
2.112	6-Cl	H	Oet	Et
2.113	6-Br	H	Oet	n-Propyl
2.114	6-Cl	H	Oet	n-Propyl

2.115	6-Br	H	Oet	
2.116	6-Cl	H	Oet	
2.117	6-Br	H	Oet	n-Butyl
2.118	6-Cl	H	Oet	n-Butyl
2.119	6-I	H	Oet	n-Butyl
2.120	6-Br	H	Oet	i-Butyl
2.121	6-Cl	H	Oet	i-Butyl
2.122	6-Br	H	Oet	
2.123	6-Cl	H	Oet	
2.124	6-Br	H	Oet	
2.125	6-Cl	H	Oet	
2.126	6-Br	H	Oet	Cyclobutyl
2.127	6-Br	H	Oet	n-Pentyl
2.128	6-Cl	H	Oet	n-Pentyl
2.129	6-Br	H	Oet	Cyclopentyl
2.130	6-Br	H	Oet	n-Hexyl
2.131	6-Br	H	Oet	Cyclohexyl
2.132	6-Br	H	Oet	Phenyl
2.133	6-Br	H	Oet	4-Chloro-phenyl
2.134	6-Cl	H	Oet	4-Chloro-phenyl
2.135	6-Br	H	Oet	4-Phenoxy-phenyl
2.136	6-Br	H	O-n-Propyl	Me

2.137	6-Cl	H	O-n-Propyl	Et
2.138	6-Br	H	O-n-Propyl	n-Propyl
2.139	6-Cl	H	O-n-Propyl	n-Propyl
2.140	6-Br	H	O-n-Propyl	
2.141	6-Cl	H	O-n-Propyl	
2.142	6-Br	H	O-n-Propyl	n-Butyl
2.143	6-Cl	H	O-n-Propyl	n-Butyl
2.144	6-Br	H	O-n-Propyl	i-Butyl
2.145	6-Cl	H	O-n-Propyl	i-Butyl
2.146	6-Br	H	O-n-Propyl	
2.147	6-Cl	H	O-n-Propyl	
2.148	6-Br	H	O-n-Propyl	
2.149	6-Cl	H	O-n-Propyl	
2.150	6-Br	H	O-n-Propyl	Cyclobutyl
2.151	6-Br	H	O-n-Propyl	n-Pentyl
2.152	6-Cl	H	O-n-Propyl	n-Pentyl
2.153	6-Br	H	O-n-Propyl	Cyclopentyl
2.154	6-Br	H	O-n-Propyl	n-Hexyl
2.155	6-Br	H	O-n-Propyl	Cyclohexyl
2.156	6-Br	H	O-n-Propyl	Phenyl
2.157	6-Br	H	O-n-Propyl	4-Chloro-phenyl
2.158	6-Cl	H	O-n-Propyl	4-Chloro-phenyl

2.159	6-Br	H	O-n-Propyl	4-Phenoxy-phenyl
2.160	6-Br	H	Et	CH_2OMe
2.161	6-Cl	H	Et	CH_2OMe
2.162	6-Br	H	n-Propyl	CH_2OMe
2.163	6-Cl	H	n-Propyl	CH_2OMe
2.164	6-Br	H	n-Butyl	CH_2OMe
2.165	6-Cl	H	n-Butyl	CH_2OMe
2.166	6-Br	H		CH_2OMe
2.167	6-Br	H	n-Pentyl	CH_2OMe
2.168	6-Br	H	Et	CH_2OEt
2.169	6-Cl	H	Et	CH_2OEt
2.170	6-Br	H	n-Propyl	CH_2OEt
2.171	6-Cl	H	n-Propyl	CH_2OEt
2.172	6-Br	H	n-Butyl	CH_2OEt
2.173	6-Cl	H	n-Butyl	CH_2OEt
2.174	6-Br	H		CH_2OEt
2.175	6-Br	H	n-Pentyl	CH_2OEt
2.176	6-Br	H	n-Prpyl	CH_2CN
2.177	6-Br	H	n-Butyl	CH_2CN
2.178	6-Br	H	n-Propyl	t-Butyl
2.179	6-Br	H	n-Propyl	t-Butyl
2.180	6-Br	H	n-Propyl	CF_3
2.181	6-Br	H	n-Butyl	CF_3

Tabelle 3: A = Thienyl[2.3-d]



cmpd. No.	R_1	R_2	R_3	R_4	phys. data m.p.°C
3.1	Cl	H	Me	Me	139-141
3.2	Cl	H	Me	Et	
3.3	Br	H	Me	n-Propyl	
3.4	Cl	H	Me	n-Propyl	
3.5	Br	H	Me	n-Butyl	
3.6	Cl	H	Me	n-Butyl	63-65
3.7	Br	H	Me	i-Butyl	
3.8	Cl	H	Me	i-Butyl	87-89
3.9	Br	H	Me	n-Pentyl	
3.10	Br	H	Me		
3.11	Cl	H	Me		
3.12	Br	H	Et	Me	
3.13	Cl	H	Et	Et	
3.14	Br	H	Et	n-Propyl	
3.15	Cl	H	Et	n-Propyl	80-82
3.16	Br	H	Et	n-Butyl	
3.17	Cl	H	Et	n-Butyl	Oil, ^{1}H-NMR
3.18	Br	H	Et	i-Butyl	
3.19	Cl	H	Et	i-Butyl	
3.20	Br	H	Et	n-Pentyl	
3.21	Br	H	Et		
3.22	Cl	H	Et		

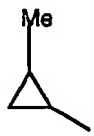
3.23	Br	H	n-Propyl	Me	
3.24	Cl	H	n-Propyl	Et	
3.25	Br	H	n-Propyl	n-Propyl	
3.26	Cl	H	n-Propyl	n-Propyl	74-76
3.27	I	H	n-Propyl	n-Propyl	
3.28	Br	H	n-Propyl		
3.29	Cl	H	n-Propyl		
3.30	Br	H	n-Propyl	n-Butyl	63-66
3.31	Cl	H	n-Propyl	n-Butyl	67-69
3.32	I	H	n-Propyl	n-Butyl	
3.33	Br	H	n-Propyl	i-Butyl	
3.34	Cl	H	n-Propyl	i-Butyl	Oil, ^{1}H-NMR
3.35	Br	H	n-Propyl		
3.36	Cl	H	n-Propyl		Oil, ^{1}H-NMR
3.37	Br	H	n-Propyl	Me 	
3.38	Cl	H	n-Propyl	Me 	
3.39	Br	H	n-Propyl	Cyclobutyl	
3.40	Br	H	n-Propyl	n-Pentyl	
3.41	Cl	H	n-Propyl	n-Pentyl	
3.42	Br	H	n-Propyl	Cyclopentyl	
3.43	Br	H	n-Propyl	n-Hexyl	
3.44	Br	H	n-Propyl	Cyclohexyl	
3.45	Br	H	n-Propyl	Phenyl	
3.46	Br	H	n-Propyl	4-Chloro-phenyl	

3.47	Cl	H	n-Propyl	4-Chloro-phenyl	126-128
3.48	Br	H	n-Propyl	4-Phenoxy-phenyl	
3.49	Br	H	n-Butyl	Me	
3.50	Cl	H	n-Butyl	Et	
3.51	Br	H	n-Butyl	n-Propyl	
3.52	Cl	H	n-Butyl	n-Propyl	Oil
3.53	I	H	n-Butyl	n-Propyl	
3.54	I	H	n-Butyl	n-Propyl	
3.55	Br	H	n-Butyl		
3.56	Cl	H	n-Butyl		54-56
3.57	I	H	n-Butyl		
3.58	Br	H	n-Butyl	n-Butyl	Oil
3.59	Cl	H	n-Butyl	n-Butyl	57-58
3.60	I	H	n-Butyl	n-Butyl	
3.61	Br	H	n-Butyl	i-Butyl	
3.62	Cl	H	n-Butyl	i-Butyl	
3.63	Br	H	n-Butyl		
3.64	Cl	H	n-Butyl		
3.65	I	H	n-Butyl		
3.66	Br	H	n-Butyl	Me 	
3.67	Cl	H	n-Butyl	Me 	

3.68	Br	H	n-Butyl	Cyclobutyl	
3.69	Br	H	n-Butyl	n-Pentyl	
3.70	Cl	H	n-Butyl	n-Pentyl	
3.71	Br	H	n-Butyl	Cyclopentyl	
3.72	Br	H	n-Butyl	n-Hexyl	
3.73	Br	H	n-Butyl	Cyclohexyl	
3.74	Cl	H	n-Butyl	Phenyl	
3.75	Br	H	n-Butyl	4-Chloro-phenyl	
3.76	Cl	H	n-Butyl	4-Chloro-phenyl	
3.77	Br	H	n-Butyl	4-Phenoxy-phenyl	
3.78	Br	H	i-Butyl	n-Propyl	
3.79	Cl	H	i-Butyl	n-Propyl	Oil, ^{1}H-NMR
3.80	Br	H	i-Butyl	n-Butyl	
3.81	Cl	H	i-Butyl	n-Butyl	
3.82	Br	H		n-Propyl	
3.83	Cl	H		n-Propyl	
3.84	Cl	H		n-Propyl	
3.85	Br	H		n-Butyl	
3.86	Br	H	n-Pentyl	Me	
3.87	Cl	H	n-Pentyl	Et	
3.88	Br	H	n-Pentyl	n-Propyl	
3.89	Cl	H	n-Pentyl	n-Propyl	
3.90	Br	H	n-Pentyl		
3.91	Cl	H	n-Pentyl		
3.92	Br	H	n-Pentyl	n-Butyl	

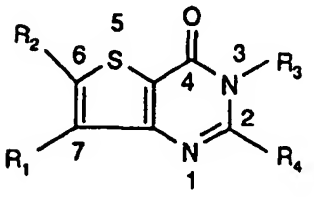
3.93	Cl	H	n-Pentyl	n-Butyl
3.94	I	H	n-Pentyl	n-Butyl
3.95	Br	H	n-Pentyl	i-Butyl
3.96	Cl	H	n-Pentyl	i-Butyl
3.97	Br	H	n-Pentyl	
3.98	Cl	H	n-Pentyl	
3.99	Br	H	n-Pentyl	
3.100	Cl	H	n-Pentyl	
3.101	Cl	H	n-Pentyl	Cyclobutyl
3.102	Br	H	n-Pentyl	n-Pentyl
3.103	Cl	H	n-Pentyl	n-Pentyl
3.104	Cl	H	n-Pentyl	Cyclopentyl
3.105	Br	H	n-Pentyl	n-Hexyl
3.106	Cl	H	n-Pentyl	Cyclohexyl
3.107	Br	H	n-Pentyl	Phenyl
3.108	Br	H	n-Pentyl	4-Chloro-phenyl
3.109	Cl	H	n-Pentyl	4-Chloro-phenyl
3.110	Br	H	n-Pentyl	4-Phenoxy-phenyl
3.111	Br	H	OEt	Me
3.112	Cl	H	OEt	Et
3.113	Br	H	OEt	n-Propyl
3.114	Cl	H	OEt	n-Propyl

3.115	Br	H	OEt		
3.116	Cl	H	OEt		
3.117	Br	H	OEt	n-Butyl	75-77
3.118	Cl	H	OEt	n-Butyl	66-69
3.119	I	H	OEt	n-Butyl	
3.120	Br	H	OEt	i-Butyl	
3.121	Cl	H	OEt	i-Butyl	
3.122	Br	H	OEt		
3.123	Cl	H	OEt		
3.124	Br	H	OEt		
3.125	Cl	H	OEt		
3.126	Br	H	OEt	Cyclobutyl	
3.127	Br	H	OEt	n-Pentyl	
3.128	Cl	H	OEt	n-Pentyl	
3.129	Br	H	OEt	Cyclopentyl	
3.130	Br	H	OEt	n-Hexyl	
3.131	Br	H	OEt	Cyclohexyl	
3.132	Br	H	OEt	Phenyl	
3.133	Br	H	OEt	4-Chloro-phenyl	
3.134	Cl	H	OEt	4-Chloro-phenyl	
3.135	Cl	H	OEt	4-Phenoxy-phenyl	
3.136	Br	H	O-n-Propyl	Me	

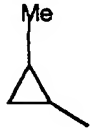
3.137	Cl	H	O-n-Propyl	Et
3.138	Br	H	O-n-Propyl	n-Propyl
3.139	Cl	H	O-n-Propyl	n-Propyl
3.140	Br	H	O-n-Propyl	
3.141	Cl	H	O-n-Propyl	
3.142	Br	H	O-n-Propyl	n-Butyl
3.143	Cl	H	O-n-Propyl	n-Butyl
3.144	Br	H	O-n-Propyl	i-Butyl
3.145	Cl	H	O-n-Propyl	i-Butyl
3.146	Br	H	O-n-Propyl	
3.147	Cl	H	O-n-Propyl	
3.148	Br	H	O-n-Propyl	
3.149	Cl	H	O-n-Propyl	
3.150	Br	H	O-n-Propyl	Cyclobutyl
3.151	Br	H	O-n-Propyl	n-Pentyl
3.152	Cl	H	O-n-Propyl	n-Pentyl
3.153	Br	H	O-n-Propyl	Cyclopentyl
3.154	Cl	H	O-n-Propyl	n-Hexyl
3.155	Br	H	O-n-Propyl	Cyclohexyl
3.156	Cl	H	O-n-Propyl	Phenyl
3.157	Br	H	O-n-Propyl	4-Chloro-phenyl
3.158	Cl	H	O-n-Propyl	4-Chloro-phenyl

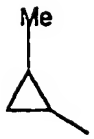
3.159	Br	H	O-n-Propyl	4-Phenoxy-phenyl	
3.160	Br	H	Et	CH_2OMe	
3.161	Cl	H	Et	CH_2OMe	
3.162	Br	H	n-Propyl	CH_2OMe	
3.163	Cl	H	n-Propyl	CH_2OMe	Oil, ^{1}H-NMR
3.164	Br	H	n-Butyl	CH_2OMe	
3.165	Cl	H	n-Butyl	CH_2OMe	
3.166	Br	H		CH_2OMe	
3.167	Br	H	n-Pentyl	CH_2OMe	
3.168	Br	H	Et	CH_2OEt	
3.169	Cl	H	Et	CH_2OEt	
3.170	Br	H	n-Propyl	CH_2OEt	
3.171	Cl	H	n-Propyl	CH_2OEt	40-41
3.172	Br	H	n-Butyl	CH_2OEt	
3.173	Cl	H	n-Butyl	CH_2OEt	
3.174	Br	H		CH_2OEt	
3.175	Br	H	n-Pentyl	CH_2OEt	
3.176	Br	H	n-Propyl	CH_2CN	
3.177	Cl	H	n-Butyl	CH_2CN	
3.178	Br	H	n-Propyl	t-Butyl	
3.179	Cl	H	n-Propyl	t-Butyl	
3.180	Br	H	n-Propyl	CF_3	
3.181	Cl	H	n-Butyl	CF_3	
3.182	Cl	H	n-Pentyl	CF_3	
3.183	Cl	Cl	n-Propyl	n-Propyl	
3.184	Cl	Cl	n-Propyl	n-Butyl	
3.185	Br	Br	n-Propyl	n-Butyl	
3.186	Br	Br	n-Butyl	n-Butyl	

Tabelle 4: A=Thienyl[3.2-d]



Cmpd. No.	R_1	R_2	R_3	R_4	phys. data
4.1	Br	H	Me	Me	
4.2	H	Cl	Me	Et	
4.3	Br	H	Me	n-Propyl	
4.4	H	Cl	Me	n-Propyl	
4.5	H	Cl	Me	n-Propyl	
4.6	Br	H	Me	n-Butyl	
4.7	H	Cl	Me	n-Butyl	
4.8	H	Cl	Me	n-Butyl	
4.9	Br	H	Me	i-Butyl	
4.10	H	Cl	Me	i-Butyl	
4.11	Br	H	Me	n-Pentyl	
4.12	Br	H	Me		
4.13	H	Cl	Me		
4.14	Br	H	Et	Me	
4.15	H	Cl	Et	Et	
4.16	Br	H	Et	n-Propyl	
4.17	H	Cl	Et	n-Propyl	
4.18	H	Cl	Et	n-Propyl	
4.19	Br	H	Et	n-Butyl	
4.20	H	Cl	Et	n-Butyl	
4.21	H	Cl	Et	n-Butyl	
4.22	Br	H	Et	i-Butyl	

4.23	H	Cl	Et	i-Butyl	
4.24	Br	H	Et	n-Pentyl	
4.25	Br	H	Et		
4.26	H	Cl	Et		
4.27	Br	H	n-Propyl	Me	
4.28	H	Cl	n-Propyl	Et	
4.29	Br	H	n-Propyl	n-Propyl	
4.30	H	Cl	n-Propyl	n-Propyl	
4.31	H	Cl	n-Propyl	n-Propyl	
4.32	H	I	n-Propyl	n-Propyl	
4.33	Br	H	n-Propyl		
4.34	H	Cl	n-Propyl		
4.35	H	Cl	n-Propyl		
4.36	Br	H	n-Propyl	n-Butyl	120-121
4.37	H	Cl	n-Propyl	n-Butyl	
4.38	H	Cl	n-Propyl	n-Butyl	
4.39	H	I	n-Propyl	n-Butyl	
4.40	Br	H	n-Propyl	i-Butyl	
4.41	H	Cl	n-Propyl	i-Butyl	
4.42	Br	H	n-Propyl		
4.43	H	Cl	n-Porpyl		
4.44	H	Cl	n-Propyl		
4.45	H	Cl	n-Propyl	Me 	

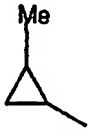
4.46	H	Cl	n-Propyl	
4.47	Br	H	n-Propyl	Cyclobutyl
4.48	Br	H	n-Propyl	n-Pentyl
4.49	H	Cl	n-Propyl	n-Pentyl
4.50	H	Cl	n-Propyl	n-Pentyl
4.51	Br	H	n-Propyl	Cyclopentyl
4.52	Br	H	n-Propyl	n-Hexyl
4.53	Br	H	n-Propyl	Cyclohexyl
4.54	Br	H	n-Propyl	Phenyl
4.55	Br	H	n-Propyl	4-Chloro-phenyl
4.55	H	Cl	n-Propyl	4-Chloro-phenyl
4.56	Br	H	n-Propyl	4-Phenoxy-phenyl
4.57	Br	H	n-Butyl	Me
4.58	H	Cl	n-Butyl	Et
4.59	Br	H	n-Butyl	n-Propyl
4.60	H	Cl	n-Butyl	n-Propyl
4.61	H	Cl	n-Butyl	n-Propyl
4.62	H	I	n-Butyl	n-Propyl
4.62	Br	H	n-Butyl	
4.63	H	Cl	n-Butyl	
4.64	H	Cl	n-Butyl	
4.65	Br	H	n-Butyl	n-Butyl
4.66	H	Cl	n-Butyl	n-Butyl
4.67	H	Cl	n-Butyl	n-Butyl
4.68	H	I	n-Butyl	n-Butyl
4.69	Br	H	n-Butyl	i-Butyl

4.70	H	Cl	n-Butyl	i-Butyl
4.71	Br	H	n-Butyl	
4.72	H	Cl	n-Butyl	
4.73	H	Cl	n-Butyl	
4.74	Br	H	n-Butyl	Me 
4.75	H	Cl	n-Butyl	Me 
4.76	Br	H	n-Butyl	Cyclobutyl
4.77	Br	H	n-Butyl	n-Pentyl
4.78	H	Cl	n-Butyl	n-Pentyl
4.79	H	Cl	n-Butyl	n-Pentyl
4.80	Br	H	n-Butyl	Cyclopentyl
4.81	Br	H	n-Butyl	n-Hexyl
4.82	Br	H	n-Butyl	Cyclohexyl
4.83	Br	H	n-Butyl	Phenyl
4.84	Br	H	n-Butyl	4-Chloro-phenyl
4.85	H	Cl	n-Butyl	4-Chloro-phenyl
4.86	Br	H	n-Butyl	4-Phenoxy-phenyl
4.87	Br	H	i-Butyl	n-Propyl
4.88	H	Cl	i-Butyl	n-Propyl
4.89	Br	H	i-Butyl	n-Butyl
4.90	H	Cl	i-Butyl	n-Butyl

4.91	Br	H		n-Propyl
4.92	H	Cl		n-Propyl
4.93	Br	H		n-Propyl
4.94	Br	H		n-Butyl
4.95	Br	H	n-Pentyl	Me
4.96	H	Cl	n-Pentyl	Et
4.97	Br	H	n-Pentyl	n-Propyl
4.98	Cl	H	n-Pentyl	n-Propyl
4.99	H	Cl	n-Pentyl	n-Propyl
4.100	H	I	n-Pentyl	n-Propyl
4.101	Br	H	n-Pentyl	
4.102	H	Cl	n-Pentyl	
4.103	H	Cl	n-Pentyl	
4.104	Br	H	n-Pentyl	n-Butyl
4.105	H	Cl	n-Pentyl	n-Butyl
4.106	H	Cl	n-Pentyl	n-Butyl
4.107	H	I	n-Pentyl	n-Butyl
4.108	Br	H	n-Pentyl	i-Butyl
4.109	H	Cl	n-Pentyl	i-Butyl
4.110	Br	H	n-Pentyl	
4.111	H	Cl	n-Pentyl	
4.112	H	Cl	n-Pentyl	

4.113	Br	H	n-Pentyl	
4.114	H	Cl	n-Pentyl	
4.115	Br	H	n-Pentyl	Cyclobutyl
4.116	Br	H	n-Pentyl	n-Pentyl
4.117	Cl	Cl	n-Pentyl	n-Pentyl
4.118	H	Cl	n-Pentyl	n-Pentyl
4.119	Br	H	n-Pentyl	Cyclopentyl
4.120	Br	H	n-Pentyl	n-Hexyl
4.121	Br	H	n-Pentyl	Cyclohexyl
4.122	Br	H	n-Pentyl	Phenyl
4.123	Br	H	n-Pentyl	4-Chloro-phenyl
4.124	H	Cl	n-Pentyl	4-Chloro-phenyl
4.125	Br	H	n-Pentyl	4-Phenoxy-phenyl
4.126	Br	H	OEt	Me
4.127	Cl	H	OEt	Et
4.128	Br	H	OEt	n-Propyl
4.129	H	Cl	OEt	n-Propyl
4.130	H	Cl	OEt	n-Propyl
4.131	H	I	OEt	n-Propyl
4.132	Br	H	OEt	
4.133	H	Cl	OEt	
4.134	H	Cl	OEt	
4.135	Br	H	OEt	n-Butyl

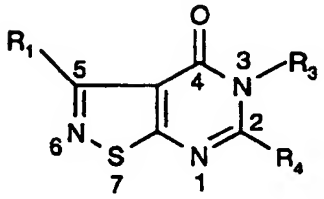
4.136	H	Cl	OEt	n-Butyl
4.137	H	Cl	OEt	n-Butyl
4.138	H	I	OEt	n-Butyl
4.139	Br	H	OEt	i-Butyl
4.140	H	Cl	OEt	i-Butyl
4.141	Br	H	OEt	
4.142	H	Cl	OEt	
4.143	H	Cl	OEt	
4.144	Br	H	OEt	
4.145	H	Cl	OEt	
4.146	Br	H	OEt	Cyclobutyl
4.147	Br	H	OEt	n-Pentyl
4.148	H	Cl	OEt	n-Pentyl
4.149	H	Cl	OEt	n-Pentyl
4.150	Br	H	OEt	Cyclopentyl
4.151	Br	H	OEt	n-Hexyl
4.152	Br	H	OEt	Cyclohexyl
4.153	Br	H	OEt	Phenyl
4.154	Br	H	OEt	4-Chloro-phenyl
4.155		Cl	OEt	4-Chloro-phenyl
4.156	Br	H	OEt	4-Phenoxy-phenyl
4.157	Br	H	O-n-Propyl	Me

4.158	H	Cl	O-n-Propyl	Et
4.159	Br	H	O-n-Propyl	n-Propyl
4.160	H	Cl	O-n-Propyl	n-Propyl
4.161	H	Cl	O-n-Propyl	n-Propyl
4.162	H	I	O-n-Propyl	n-Propyl
4.163	Br	H	O-n-Propyl	
4.164	H	Cl	O-n-Propyl	
4.165	H	Cl	O-n-Propyl	
4.166	Br	H	O-n-Propyl	n-Butyl
4.167	H	Cl	O-n-Propyl	n-Butyl
4.168	H	Cl	O-n-Propyl	n-Butyl
4.169	H	II	O-n-Propyl	n-Butyl
4.170	Br	H	O-n-Propyl	i-Butyl
4.171	H	Cl	O-n-Propyl	i-Butyl
4.172	Br	H	O-n-Propyl	
4.173	H	Cl	O-n-Propyl	
4.174	H	Cl	O-n-Propyl	
4.175	Br	H	O-n-Propyl	Me 
4.176	H	Cl	O-n-Propyl	Me 
4.177	Br	H	O-n-Propyl	Cyclobutyl
4.178	Br	H	O-n-Propyl	n-Pentyl
4.179	H	Cl	O-n-Propyl	n-Pentyl
4.180	H	Cl	O-n-Propyl	n-Pentyl

4.181	Br	H	O-n-Propyl	Cyclopentyl
4.182	Br	H	O-n-Propyl	n-Hexyl
4.183	Br	H	O-n-Propyl	Cyclohexyl
4.184	Br	H	O-n-Propyl	Phenyl
4.185	Br	H	O-n-Propyl	4-Chloro-phenyl
4.186	H	Cl	O-n-Propyl	4-Chloro-phenyl
4.187	Br	H	O-n-Propyl	4-Phenoxy-phenyl
4.188	Br	H	Et	CH_2OMe
4.189	H	Cl	Et	CH_2OMe
4.190	Br	H	n-Propyl	CH_2OMe
4.191	H	Cl	n-Propyl	CH_2OMe
4.192	H	Cl	n-Propyl	CH_2OMe
4.193	Br	H	n-Butyl	CH_2OMe
4.194	H	Cl	n-Butyl	CH_2OMe
4.195	Br	H		CH_2OMe
4.195	Br	H	n-Pentyl	CH_2OMe
4.196	Br	H	Et	CH_2OEt
4.197	H	Cl	Et	CH_2OEt
4.198	Br	H	n-Propyl	CH_2OEt
4.199	H	Cl	n-Propyl	CH_2OEt
4.200	H	Cl	n-Propyl	CH_2OEt
4.201	Br	H	n-Butyl	CH_2OEt
4.202	H	Cl	n-Butyl	CH_2OEt
4.203	Br	H		CH_2OEt
4.204	Br	H	n-Pentyl	CH_2OEt
4.205	Br	H	n-Propyl	CH_2CN
4.206	Br	H	n-Butyl	CH_2CN

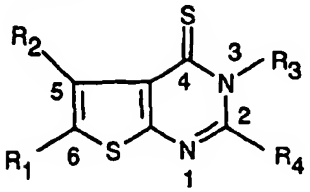
4.207	Br	H	n-Propyl	t-Butyl
4.208	Br	H	n-Propyl	t-Butyl
4.209	H	Cl	n-Propyl	CF_3
4.210	Br	H	n-Propyl	CF_3
4.211	H	Cl	n-Butyl	CF_3
4.212	Br	H	n-Butyl	CF_3
4.213	Cl	Cl	n-Propyl	n-Propyl
4.214	Cl	Cl	n-Propyl	n-Butyl
4.215	Br	Br	n-Propyl	n-Butyl
4.216	Br	Br	*n*-Butyl	n-Butyl

Tabelle 5: A= Thiazolyl



Cmpd. No.	R_1	R_3	R_4	phys. data
5.1	H	Et	n-Propyl	
5.2	H	n-Propyl	n-Propyl	
5.3	H	n-Propyl	n-Butyl	
5.4	H	n-Butyl	n-Butyl	
5.5	Me	n-Propyl	n-Propyl	
5.6	Me	n-Propyl	n-Butyl	
5.7	Me	n-Butyl	n-Butyl	
5.8	H	n-Propyl	Phenyl	

Tabelle 7: A = Thienyl[2.3-d]



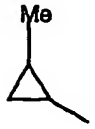
cmpd. No.	R_1	R_2	R_3	R_4	phys. data m.p.°C
7.1	Br	H	Me	Me	
7.2	Cl	H	Me	Et	
7.3	Br	H	Me	n-Propyl	
7.4	Cl	H	Me	n-Propyl	
7.5	Br	H	Me	n-Butyl	
7.6	Cl	H	Me	n-Butyl	113-114
7.7	Br	H	Me	i-Butyl	
7.8	Cl	H	Me	i-Butyl	
7.9	Br	H	Me	n-Pentyl	
7.10	Br	H	Me		
7.11	Cl	H	Me		
7.12	Br	H	Et	Me	
7.13	Cl	H	Et	Et	
7.14	Br	H	Et	n-Propyl	
7.15	Cl	H	Et	n-Propyl	
7.16	Br	H	Et	n-Butyl	
7.17	Cl	H	Et	n-Butyl	
7.18	Br	H	Et	i-Butyl	
7.19	Cl	H	Et	i-Butyl	
7.20	Br	H	Et	n-Pentyl	
7.21	Br	H	Et		
7.22	Cl	H	Et		

7.23	Br	H	n-Propyl	Me	
7.24	Cl	H	n-Propyl	Et	
7.25	Br	H	n-Propyl	n-Propyl	
7.26	Cl	H	n-Propyl	n-Propyl	
7.27	I	H	n-Propyl	n-Propyl	
7.28	Br	H	n-Propyl		
7.29	Cl	H	n-Propyl		
7.30	Br	H	n-Propyl	n-Butyl	
7.31	Cl	H	n-Propyl	n-Butyl	Oil, ^{1}H-NMR
7.32	I	H	n-Propyl	n-Butyl	
7.33	Br	H	n-Propyl	i-Butyl	
7.34	Cl	H	n-Propyl	i-Butyl	57-60
7.35	Br	H	n-Propyl		
7.36	Cl	H	n-Propyl		
7.37	Br	H	n-Propyl		
7.38	Cl	H	n-Propyl		
7.39	Br	H	n-Propyl	Cyclobutyl	
7.40	Br	H	n-Propyl	n-Pentyl	
7.41	Cl	H	n-Propyl	n-Pentyl	
7.42	Br	H	n-Propyl	Cyclopentyl	
7.43	Br	H	n-Propyl	n-Hexyl	
7.44	Br	H	n-Propyl	Cyclohexyl	
7.45	Br	H	n-Propyl	Phenyl	
7.46	Br	H	n-Propyl	4-Chloro-phenyl	

7.47	Cl	H	n-Propyl	4-Chloro-phenyl
7.48	Br	H	n-Propyl	4-Phenoxy-phenyl
7.49	Br	H	n-Butyl	Me
7.50	Cl	H	n-Butyl	Et
7.51	Br	H	n-Butyl	n-Propyl
7.52	Cl	H	n-Butyl	n-Propyl
7.53	I	H	n-Butyl	n-Propyl
7.54	I	H	n-Butyl	n-Propyl
7.55	Br	H	n-Butyl	
7.56	Cl	H	n-Butyl	
7.57	I	H	n-Butyl	
7.58	Br	H	n-Butyl	n-Butyl
7.59	Cl	H	n-Butyl	n-Butyl
7.60	I	H	n-Butyl	n-Butyl
7.61	Br	H	n-Butyl	i-Butyl
7.62	Cl	H	n-Butyl	i-Butyl
7.63	Br	H	n-Butyl	
7.64	Cl	H	n-Butyl	
7.65	I	H	n-Butyl	
7.66	Br	H	n-Butyl	Me 
7.67	Cl	H	n-Butyl	Me 

7.68	Br	H	n-Butyl	Cyclobutyl
7.69	Br	H	n-Butyl	n-Pentyl
7.70	Cl	H	n-Butyl	n-Pentyl
7.71	Br	H	n-Butyl	Cyclopentyl
7.72	Br	H	n-Butyl	n-Hexyl
7.73	Br	H	n-Butyl	Cyclohexyl
7.74	Cl	H	n-Butyl	Phenyl
7.75	Br	H	n-Butyl	4-Chloro-phenyl
7.76	Cl	H	n-Butyl	4-Chloro-phenyl
7.77	Br	H	n-Butyl	4-Phenoxy-phenyl
7.78	Br	H	i-Butyl	n-Propyl
7.79	Cl	H	i-Butyl	n-Propyl
7.80	Br	H	i-Butyl	n-Butyl
7.81	Cl	H	i-Butyl	n-Butyl
7.82	Br	H		n-Propyl
7.83	Cl	H		n-Propyl
7.84	Cl	H		n-Propyl
7.85	Br	H		n-Butyl
7.86	Br	H	n-Pentyl	Me
7.87	Cl	H	n-Pentyl	Et
7.88	Br	H	n-Pentyl	n-Propyl
7.89	Cl	H	n-Pentyl	n-Propyl
7.90	Br	H	n-Pentyl	
7.91	Cl	H	n-Pentyl	
7.92	Br	H	n-Pentyl	n-Butyl

7.93	Cl	H	n-Pentyl	n-Butyl
7.94	I	H	n-Pentyl	n-Butyl
7.95	Br	H	n-Pentyl	i-Butyl
7.96	Cl	H	n-Pentyl	i-Butyl
7.97	Br	H	n-Pentyl	
7.98	Cl	H	n-Pentyl	
7.99	Br	H	n-Pentyl	
7.100	Cl	H	n-Pentyl	
7.101	Cl	H	n-Pentyl	Cyclobutyl
7.102	Br	H	n-Pentyl	n-Pentyl
7.103	Cl	H	n-Pentyl	n-Pentyl
7.104	Cl	H	n-Pentyl	Cyclopentyl
7.105	Br	H	n-Pentyl	n-Hexyl
7.106	Cl	H	n-Pentyl	Cyclohexyl
7.107	Br	H	n-Pentyl	Phenyl
7.108	Br	H	n-Pentyl	4-Chloro-phenyl
7.109	Cl	H	n-Pentyl	4-Chloro-phenyl
7.110	Br	H	n-Pentyl	4-Phenoxy-phenyl
7.111	Br	H	OEt	Me
7.112	Cl	H	OEt	Et
7.113	Br	H	OEt	n-Propyl
7.114	Cl	H	OEt	n-Propyl

7.115	Br	H	OEt	
7.116	Cl	H	OEt	
7.117	Br	H	OEt	n-Butyl
7.118	Cl	H	OEt	n-Butyl
7.119	I	H	OEt	n-Butyl
7.120	Br	H	OEt	i-Butyl
7.121	Cl	H	OEt	i-Butyl
7.122	Br	H	OEt	
7.123	Cl	H	OEt	
7.124	Br	H	OEt	
7.125	Cl	H	OEt	
7.126	Br	H	OEt	Cyclobutyl
7.127	Br	H	OEt	n-Pentyl
7.128	Cl	H	OEt	n-Pentyl
7.129	Br	H	OEt	Cyclopentyl
7.130	Br	H	OEt	n-Hexyl
7.131	Br	H	OEt	Cyclohexyl
7.132	Br	H	OEt	Phenyl
7.133	Br	H	OEt	4-Chloro-phenyl
7.134	Cl	H	OEt	4-Chloro-phenyl
7.135	Cl	H	OEt	4-Phenoxy-phenyl
7.136	Br	H	O-n-Propyl	Me

7.137	Cl	H	O-n-Propyl	Et
7.138	Br	H	O-n-Propyl	n-Propyl
7.139	Cl	H	O-n-Propyl	n-Propyl
7.140	Br	H	O-n-Propyl	
7.141	Cl	H	O-n-Propyl	
7.142	Br	H	O-n-Propyl	n-Butyl
7.143	Cl	H	O-n-Propyl	n-Butyl
7.144	Br	H	O-n-Propyl	i-Butyl
7.145	Cl	H	O-n-Propyl	i-Butyl
7.146	Br	H	O-n-Propyl	
7.147	Cl	H	O-n-Propyl	
7.148	Br	H	O-n-Propyl	
7.149	Cl	H	O-n-Propyl	
7.150	Br	H	O-n-Propyl	Cyclobutyl
7.151	Br	H	O-n-Propyl	n-Pentyl
7.152	Cl	H	O-n-Propyl	n-Pentyl
7.153	Br	H	O-n-Propyl	Cyclopentyl
7.154	Cl	H	O-n-Propyl	n-Hexyl
7.155	Br	H	O-n-Propyl	Cyclohexyl
7.156	Cl	H	O-n-Propyl	Phenyl
7.157	Br	H	O-n-Propyl	4-Chloro-phenyl
7.158	Cl	H	O-n-Propyl	4-Chloro-phenyl

7.159	Br	H	O-n-Propyl	4-Phenoxy-phenyl
7.160	Br	H	Et	CH_2OMe
7.161	Cl	H	Et	CH_2OMe
7.162	Br	H	n-Propyl	CH_2OMe
7.163	Cl	H	n-Propyl	CH_2OMe
7.164	Br	H	n-Butyl	CH_2OMe
7.165	Cl	H	n-Butyl	CH_2OMe
7.166	Br	H		CH_2OMe
7.167	Br	H	n-Pentyl	CH_2OMe
7.168	Br	H	Et	CH_2OEt
7.169	Cl	H	Et	CH_2OEt
7.170	Br	H	n-Propyl	CH_2OEt
7.171	Cl	H	n-Propyl	CH_2OEt
7.172	Br	H	n-Butyl	CH_2OEt
7.173	Cl	H	n-Butyl	CH_2OEt
7.174	Br	H		CH_2OEt
7.175	Br	H	n-Pentyl	CH_2OEt
7.176	Br	H	n-Propyl	CH_2CN
7.177	Cl	H	n-Butyl	CH_2CN
7.178	Br	H	n-Propyl	t-Butyl
7.179	Cl	H	n-Propyl	t-Butyl
7.180	Br	H	n-Propyl	CF_3
7.181	Cl	H	n-Butyl	CF_3
7.182	Cl	H	n-Pentyl	CF_3
7.183	Cl	Cl	n-Propyl	n-Propyl
7.184	Cl	Cl	n-Propyl	n-Butyl
7.185	Br	Br	n-Propyl	n-Butyl
7.186	Br	Br	n-Butyl	n-Butyl

[0066] Examples for specific formulations-combination are as disclosed e.g. in WO 97/33890, e.g. for wettable powders, emulsifiable concentrates, dusts, extruder granules, coated granules, solutions and suspension concentrates.

Biological Examples: Fungidical actions

Example B-1: Action against Colletotrichum lagenarium on cucumbers

[0067] After a growth period of 2 weeks, cucumber plants are sprayed with an aqueous spray mixture (concentration 0.002%) prepared from a wettable powder formulation of the test compound and infected 2 days later with a spore suspension (1.5×10^5 spores/ml) of the fungus and incubated for 36 hours at 23°C and high humidity. Incubation is then continued at normal humidity and c. 22°C. Evaluation of the fungal infestation is made 8 days after infection.
The compounds of the Tables 2-7 show good to excellent activity, preferably the compounds 2.30, 3.1, 3.6, 3.8, 3.15, 3.17, 3.26, 3.30, 3.31, 3.47, 3.52, 3.56, 3.58, 3.59, 3.79, 3.117, 3.118, 3.163, 3.171, 4.36, 7.6, 7.31 and 7.34.

Example B-2: Residual-protective action against Venturia inaequalis on apples

[0068] Apple cuttings with fresh shoots 10 to 20 cm long are sprayed to drip point with a spray mixture (0.02% a.i.) prepared from a wettable powder formulation of the test compound. The plants are infected 24 hours later with a conidia suspension of the fungus. The plants are then incubated for 5 days at 90 to 100 % relative humidity and stood in a greenhouse for a further 10 days at 20 to 24°C. Evaluation of the fungal infestation is made 12 days after infection.
Compounds of Tables 2-7 show good activity, preferably the compounds 2.30, 3.1, 3.6, 3.8, 3.15, 3.17, 3.26, 3.30, 3.31, 3.34, 3.36, 3.47, 3.52, 3.56, 3.58, 3.59, 3.79, 3.117, 3.118, 3.163, 3.171, 4.36, 7.6, 7.31 and 7.34.

Example B-3: Action against Erysiphe graminis on barley

a) Residual-protective action

[0069] Barley plants about 8 cm in height are sprayed to drip point with a spray mixture (0.02% a.i.) prepared from a wettable powder formulation of the test compound, and the treated plants are dusted with conidia of the fungus 3 to 4 hours later. The infected plants are stood in a greenhouse at 22°C. Evaluation of the fungal infection is made 12 days after infection.

b) Systemic action

[0070] Barley plants about 8 cm in height are drenched with an aqueous spray mixture (0.002% a.i., based on the volume of the soil) prepared from a wettable powder formulation of the test compound. Care is taken that the spray mixture does not come into contact with the growing parts of the plants. The treated plants are dusted 48 hours later with conidia of the fungus. The infected plants are then stood in a greenhouse at 22°C. Evaluation of the fungal infestation is made 12 days after infection.

[0071] Compared with the control plants, infestation of the plants treated with compounds of formula I from Tables 2-7, for example the compounds 2.30, 3.1, 3.6, 3.8, 3.15, 3.17, 3.26, 3.30, 3.31, 3.34, 3.36, 3.47, 3.52, 3.56, 3.58, 3.59, 3.79, 3.117, 3.118, 3.163, 3.171, 4.36, 7.6, 7.31 and 7.34 is 20 % or less.

Example B-4: Action against Podosphaera leucotricha on apple shoots

[0072] Apple cuttings with fresh shoots about 15cm long are sprayed with a spray mixture (0.06% a.i.). The plants are infected 24 hours later with a conidia suspension of the fungus and stood in a climatic chamber at 70% relative humidity and 20°C. Evaluation of the fugal infestation is made 12 days after infection.
Compounds of Tables 2-7 show good activity. The following compounds exhibit especially strong efficacy : 2.30, 3.1, 3.6, 3.8, 3.15, 3.17, 3.26, 3.30, 3.31, 3.34, 3.36, 3.47, 3.52, 3.56, 3.58, 3.59, 3.79, 3.117, 3.118, 3.163, 3.171, 4.36, 7.6, 7.31 and 7.34 (0-5% infestation).

Example B-5: Action against Plasmopara viticola on vines

[0073]

a) Residual-preventive action: Vine cuttings of the Chasselas variety are raised in a greenhouse. At the 10-leaf stage, 3 plants are sprayed with a spray mixture (200 ppm a.i.). After the spray coating has dried, the plants are

infected uniformly on the underside of the leaves with a spore suspension of the fungus. The plants are then kept in a humidity chamber for 8 days, after which time marked symptoms of disease are observed on the control plants. The number and size of the infected areas on the untreated plants act as an indicator of the efficacy of the tested compounds.

b) Curative action: Vine cuttings of the Chasselas variety are raised in a greenhouse and sprayed at the 10-leaf stage on the underside of the leaves with a spore suspension of Plasmopara viticola. After 24 hours in the humidity chamber, the plants are sprayed with a spray mixture (200 ppm a.i.). The plants are then kept for another 7 days in the humidity chamber. After this time the control plants exhibit symptoms of the disease. The number and size of the infected areas on the untreated plants act as an indicator of the efficacy of the tested compounds.

[0074] Compounds of Tables 2-7 show good efficacy, preferably the compounds 2.30, 3.1, 3.6, 3.8, 3.15, 3.17, 3.26, 3.30, 3.31, 3.34, 3.36, 3.47, 3.52, 3.56, 3.58, 3.59, 3.79, 3.117, 3.118, 3.163, 3.171, 4.36, 7.6, 7.31 and 7.34.

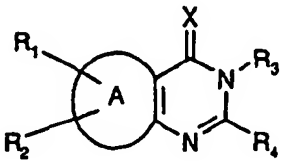
Example B-6: Action against Uncinula necator on vines

[0075] 5 week old vine cuttings are sprayed with a spray mixture (200 ppm a.i.) prepared from a wettable powder formulation of the test compound.The plants are infected 24 hours later by conidias from strongly infested vine leafs that are shaken off over the test plants. The plants are then incubated at 26°C and 60% relative humidity. The evaluation of the fungal infestation is made ca. 14 days after infection.

Compared with the control plants, infestation of the plants treated with compounds of formula I from the Tables 2-7, for example the compounds 2.30, 3.1, 3.6, 3.8, 3.15, 3.17, 3.26, 3.30, 3.31, 3.34, 3.36, 3.47, 3.52, 3.56, 3.58, 3.59, 3.79, 3.117, 3.118, 3.163, 3.171, 4.36, 7.6, 7.31 and 7.34 is 20 % or less.

Claims

1. A compound of formula I



(I)

wherein

A is thienyl, thiazolyl, pyridyl or pyridazinyl ;
X is oxygen or sulfur;
R_1 is hydrogen, halogen or trimethylsilyl;
R_2 is hydrogen, halogen or trimethylsilyl; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_8alkyl, C_1-C_8alkenyl, C_1-C_8alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen, C_1-C_6alkoxy or C_1-C_6haloalkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_6alkoxy; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_8alkyl, C_1-C_8alkenyl, C_1-C_8alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen, cyano, C_1-C_6alkoxy or C_1-C_6haloalkoxy; nitro; -CO-C_1-C_6alkyl; C_3-C_6cycloalkyl; or phenyl, which is unsubstituted or mono to tri-substituted by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, cyano, nitro, amino, mono-C_1-C_6alkylamino, di-C_1-C_6alkyl-amino, C_1-C_6alkylthio, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy or C_1-C_6haloalkoxy.

2. A compound of formula I according to claim 1, wherein
A is thienyl.

3. A compounds of formula I according to claim 2 wherein

R_1 is hydrogen, fluorine, chlorine, bromine or iodine;
R_2 is hydrogen, fluorine, chlorine, bromine or iodine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkoxy; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_4alkyoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4haloalkoxy.

4. A compound of formula I according to claim 3, wherein

R_3 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_4cycloalkyl, fluorine, chlorine, bromine or C_1-C_4alkoxy; O-C_1-C_6alkyl; O-C_2-C_6alkenyl; O-C_2-C_6alkynyl; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_4cycloalkyl, fuorine, chlorine, bromine or C_1-C_4alkoxy; or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4halo-alkoxy, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine.

5. A compound of the formula I according to claim 4, wherein

A is thienyl[2.3-d],
X is oxygen,
R_1 is hydrogen, chlorine or bromine;
R_2 is hydrogen, chlorine or bromine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_3-C_5alkyl or O-C_1-C_4alkyl;
R_4 is C_2-C_5alkyl or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl or phenoxy and in which phenoxy is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine.

6. A compound of the formula I according to claim 4, wherein

A is thienyl[2.3-d],
X is sulfur,
R_1 is hydrogen, chlorine or bromine;
R_2 is hydrogen, chlorine or bromine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_3-C_5alkyl or O-C_1-C_4alkyl;
R_4 is C_2-C_5alkyl or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl or phenoxy and in which phenoxy is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine.

7. A compound of the formula I according to claim 4, wherein

A is thienyl[3.2-d],
X is oxygen,
R_1 is hydrogen, chlorine or bromine;
R_2 is hydrogen, chlorine or bromine; at least one of R_1 and R_2 is not hydrogen;
R_3 is C_3-C_5alkyl or O-C_1-C_4alkyl;
R_4 is C_2-C_5alkyl or phenyl which is unsubstituted or mono to tri-substituted by fluorine, chlorine, bromine, C_1-C_4alkyl or phenoxy and in which phenoxy is unsubstituted or mono to tri-substituted by fluorine, chlorine or bromine.

8. A compound of formula I according to claim 1, wherein
A is pyridyl.

9. A compound of formula I according to claim 1, wherein
A is thiazolyl.

10. A compound of formula I according to claim 1, wherein
A is pyridazinyl.

11. A composition for controlling and preventing pests, wherein the active ingredient is a compound as claimed in claim 1 together with a suitable carrier.

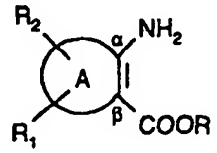
12. Use of a compound of formula I according to claim 1 for protecting plants against infestation by phytopathogenic microorganisms.

13. A method of controlling or preventing infestation of cultivated plants by phytopathogenic microorganisms by application of a compound of formula I as claimed in claim 1 to plants, to parts thereof or to the locus thereof.

14. A method according to claim 13, wherein the phytopathogenic microorganism is a fungal organism.

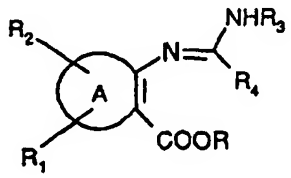
15. A method for the preparation of a compound of formula I according to claim 1, which comprises

a) converting an α-amino-β-carboalkoxyheterocycle of formula II, wherein R_1 and R_2 have the meanings stated for formula I and R is hydrogen, C_1-C_6alkyl,



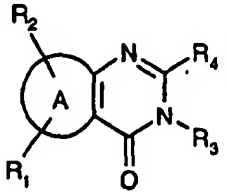
II

with $POCl_3$ in the presence of a solvent and R_4CONHR_3 into an amidine of formula III, wherein R_3 and R_4 have the meanings stated for formula I



III ;

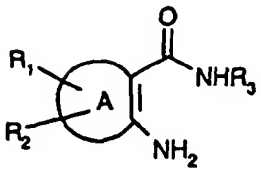
b) and treating the amidine, in the presence of a solvent and if necessary in the presence of a base, and obtaining, with ring closure, the pyrimidin-4-one derivative of formula IV



IV ;

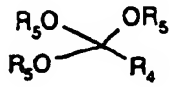
or

c) reacting an amino carboxylic acidamide of formula VI



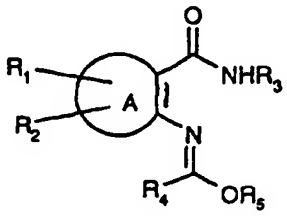
VI

wherein A, R_1, R_2 and R_3 have the meanings stated for formula I
with an orthoester of formula XIII



XIII

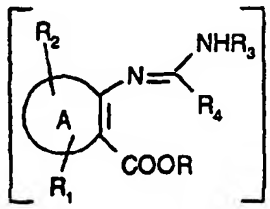
wherein R_4 has the meaning stated for formula I and R_5 is C_1-C_5alkyl,
in the presence or absence of a solvent, in the presence or absence of an acid catalyst at 20-200°C, and obtaining the pyrimidin-4-one derivative of formula IV; and
d) if the intermediate VII is formed



VII

treating the compound VII in the presence of a solvent and if necessary in the presence of a base, and obtaining with ring closure the pyrimidin-4-one derivative of formula IV.

16. A compound of formula III



III

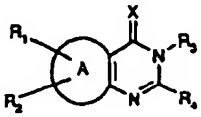
wherein

A is thienyl[2.3-d] or thienyl[3.2-d];
R_1 is hydrogen, halogen or trimethylsilyl;
R_2 is hydrogen, halogen or trimethylsilyl; and at least one of R_1 and R_2 is not hydrogen;
R_3 is C_1-C_8alkyl, C_1-C_8alkenyl, C_1-C_8alkinyl which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen, C_1-C_6alkoxy or C_1-C_6haloalkoxy; O-C_1-C_6alkyl, O-C_2-C_6alkenyl, O-C_2-C_6alkynyl, which are unsubstituted or mono to tri-substituted by C_3-C_6cycloalkyl, halogen or C_1-C_6alkoxy; N-C_1-C_6alkyl; or N=CHC_1-C_6alkyl;
R_4 is C_1-C_8alkyl, C_1-C_8alkenyl, C_1-C_8alkinyl which are unsubstituted or mono to tri-substituted by

C_3-C_6cycloalkyl, halogen, cyano, C_1-C_6alkoxy or C_1-C_6haloalkoxy; nitro; -CO-C_1-C_6alkyl; C_3-C_6cycloalkyl; or phenyl, which is unsubstituted or mono to tri-substituted by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, cyano, nitro, amino, mono-C_1-C_6alkylamino, di-C_1-C_6alkyl-amino, C_1-C_6alkylthio, phenyl or phenoxy and in which the phenyl part is unsubstituted or mono to tri-substituted by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy or C_1-C_6halo-alkoxy; and R is hydrogen or C_1-C_6alkyl.

Patentansprüche

1. Verbindung der Formel I



(I)

worin

A Thienyl, Thiazolyl, Pyridyl oder Pyridazinyl darstellt;
X Sauerstoff oder Schwefel darstellt;
R_1 Wasserstoff, Halogen oder Trimethylsilyl darstellt;
R_2 Wasserstoff, Halogen oder Trimethylsilyl darstellt, wobei mindestens einer der Reste R_1 und R_2 nicht Wasserstoff darstellt;
R_3 C_1-C_8-Alkyl, C_1-C_8-Alkenyl, C_1-C_8-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen, C_1-C_6-Alkoxy oder C_1-C_6-Halogenalkoxy ein- bis dreifach substituiert sind; O-C_1-C_6-Alkyl, O-C_2-C_6-Alkenyl, O-C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen oder C_1-C_6-Alkoxy ein- bis dreifach substituiert sind; N-C_1-C_6-Alkyl; oder N=CHC_1-C_6-Alkyl darstellt;
R_4 C_1-C_8-Alkyl, C_1-C_8-Alkenyl, C_1-C_8-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen, Cyano, C_1-C_6-Alkoxy oder C_1-C_6-Halogenalkoxy ein- bis dreifach substituiert sind; Nitro; -CO-C_1-C_6-Alkyl; C_3-C_6-Cycloalkyl; oder Phenyl, das unsubstituiert oder mit Halogen, C_1-C_6-Alkyl, C_1-C_6-Halogenalkyl, C_1-C_6-Alkoxy, C_1-C_6-Halogenalkoxy, Cyano, Nitro, Amino, Mono-C_1-C_6-alkylamino, Di-C_1-C_6-alkylamino, C_1-C_6-Alkylthio, Phenyl oder Phenoxy ein- bis dreifach substituiert ist, und worin der Phenylteil unsubstituiert oder mit Halogen, C_1-C_6-Alkyl, C_1-C_6-Halogenalkyl, C_1-C_6-Alkoxy oder C_1-C_6-Halogenalkoxy einbis dreifach substituiert ist, darstellt.

2. Verbindung der Formel I nach Anspruch 1, worin
A Thienyl darstellt.

3. Verbindungen der Formel I nach Anspruch 2, worin

R_1 Wasserstoff, Fluor, Chlor, Brom oder Jod darstellt;
R_2 Wasserstoff, Fluor, Chlor, Brom oder Jod darstellt; wobei mindestens einer der Reste R_1 und R_2 nicht Wasserstoff darstellt;
R_3 C_1-C_6-Alkyl, C_2-C_6-Alkenyl, C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen oder C_1-C_4-Alkoxy ein- bis dreifach substituiert sind; O-C_1-C_6-Alkyl, O-C_2-C_6-Alkenyl, O-C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen oder C_1-C_4-Alkoxy ein- bis dreifach substituiert sind; N-C_1-C_6-Alkyl; oder N=CHC_1-C_6-Alkyl darstellt;
R_4 C_1-C_6-Alkyl, C_2-C_6-Alkenyl, C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen oder C_1-C_4-Alkoxy ein- bis dreifach substituiert sind; oder Phenyl, das unsubstituiert oder mit Fluor, Chlor, Brom, C_1-C_4-Alkyl, C_1-C_4-Halogenalkyl, C_1-C_4-Alkoxy, C_1-C_4-Halogenalkoxy, Phenyl oder Phenoxy ein- bis dreifach substituiert ist, und worin der Phenylteil unsubstituiert oder mit Fluor, Chlor, Brom, C_1-C_4-Alkyl, C_1-C_4-Halogenalkyl, C_1-C_4-Alkoxy oder C_1-C_4-Halogenalkoxy einbis dreifach substituiert ist, darstellt.

4. Verbindung der Formel I nach Anspruch 3, worin

R_3 C_1-C_6-Alkyl, C_2-C_6-Alkenyl, C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_4-Cycloalkyl, Fluor, Chlor, Brom

oder C_1-C_4-Alkoxy ein- bis dreifach substituiert sind; O-C_1-C_6-Alkyl, O-C_2-C_6-Alkenyl, O-C_2-C_6-Alkinyl; N-C_1-C_6-Alkyl; oder N=CHC_1-C_6-Alkyl darstellt;
R_4 C_1-C_6-Alkyl, C_2-C_6-Alkenyl, C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_4-Cycloalkyl, Fluor, Chlor, Brom oder C_1-C_4-Alkoxy ein- bis dreifach substituiert sind; oder Phenyl, das unsubstituiert oder mit Fluor, Chlor, Brom, C_1-C_4-Alkyl, C_1-C_4-Halogenalkyl, C_1-C_4-Alkoxy, C_1-C_4-Halogenalkoxy, Phenyl oder Phenoxy ein- bis dreifach substituiert ist, und worin der Phenylteil unsubstituiert oder mit Fluor, Chlor oder Brom einbis dreifach substituiert ist, darstellt.

5. Verbindung der Formel I nach Anspruch 4, worin

A Thienyl[2.3-d] darstellt,
X Sauerstoff darstellt,
R_1 Wasserstoff, Chlor oder Brom darstellt;
R_2 Wasserstoff, Chlor oder Brom darstellt; wobei mindestens einer der Reste R_1 und R_2 nicht Wasserstoff darstellt;
R_3 C_3-C_5-Alkyl oder O-C_1-C_4-Alkyl darstellt;
R_4 C_2-C_5-Alkyl oder Phenyl, das unsubstituiert oder mit Fluor, Chlor, Brom, C_1-C_4-Alkyl oder Phenoxy ein- bis dreifach substituiert ist und worin Phenoxy unsubstituiert oder mit Fluor, Chlor oder Brom ein- bis dreifach substituiert ist, darstellt.

6. Verbindung der Formel I nach Anspruch 4, worin

A Thienyl[2.3-d] darstellt,
X Schwefel darstellt,
R_1 Wasserstoff, Chlor oder Brom darstellt;
R_2 Wasserstoff, Chlor oder Brom darstellt; wobei mindestens einer der Reste R_1 und R_2 nicht Wasserstoff darstellt;
R_3 C_3-C_5-Alkyl oder O-C_1-C_4-Alkyl darstellt;
R_4 C_2-C_5-Alkyl oder Phenyl, das unsubstituiert oder mit Fluor, Chlor, Brom, C_1-C_4-Alkyl oder Phenoxy ein- bis dreifach substituiert ist und wobei Phenoxy unsubstituiert oder mit Fluor, Chlor oder Brom ein- bis dreifach substituiert ist, darstellt.

7. Verbindung der Formel I nach Anspruch 4, worin

A Thienyl[3.2-d] darstellt,
X Sauerstoff darstellt,
R_1 Wasserstoff, Chlor oder Brom darstellt;
R_2 Wasserstoff, Chlor oder Brom darstellt; wobei mindestens einer der Reste R_1 und R_2 nicht Wasserstoff darstellt;
R_3 C_3-C_5-Alkyl oder O-C_1-C_4-Alkyl darstellt;
R_4 C_2-C_5-Alkyl oder Phenyl, das unsubstituiert oder mit Fluor, Chlor, Brom, C_1-C_4-Alkyl oder Phenoxy ein- bis dreifach substituiert ist und worin Phenoxy unsubstituiert oder mit Fluor, Chlor oder Brom ein- bis dreifach substituiert ist, darstellt.

8. Verbindung der Formel I nach Anspruch 1, worin A Pyridyl darstellt.

9. Verbindung der Formel I nach Anspruch 1, worin A Thiazolyl darstellt.

10. Verbindung der Formel I nach Anspruch 1, worin A Pyridazinyl darstellt.

11. Zusammensetzung zur Bekämpfung von Schädlingen und Prävention vor Schädlingen, wobei der Wirkstoff eine Verbindung nach Anspruch 1 zusammen mit einem geeigneten Träger darstellt.

12. Verwendung einer Verbindung der Formel I nach Anspruch 1 zum Schutz von Pflanzen gegen Befall durch phytopathogene Mikroorganismen.

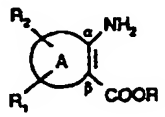
13. Verfahren zur Bekämpfung oder Prävention des Befalls von Kulturpflanzen durch phytopathogene Mikroorganismen durch Applizieren einer Verbindung der Formel I nach Anspruch 1 auf Pflanzen, Teile davon oder deren

Standort.

14. Verfahren nach Anspruch 13, wobei die phytopathogenen Mikroorganismen fungale Organismen darstellen.

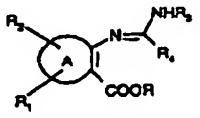
15. Verfahren zur Herstellung einer Verbindung der Formel I nach Anspruch 1, das umfasst

a) Umwandeln eines α-Amino-β-carboalkoxyheterocyclus der Formel II, worin R_1 und R_2 die in Formel I ausgewiesenen Bedeutungen aufweisen und R Wasserstoff, C_1-C_6-Alkyl, darstellt,



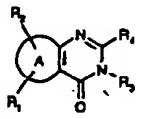
II

mit $POCl_3$ in Gegenwart eines Lösungsmittels und R_4CONHR_3 in ein Amidin der Formel III, worin R_3 und R_4 die für Formel I ausgewiesenen Bedeutungen aufweisen,



III

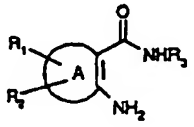
b) und Behandeln des Amidins in Gegenwart eines Lösungsmittels und, falls erforderlich, in Gegenwart einer Base, und Gewinnen, unter Ringschluss, des Pyrimidin-4-on-derivats der Formel IV



IV

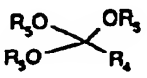
oder

c) Umsetzen eines Aminocarbonsäureamids der Formel VI



VI

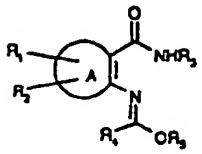
worin A, R_1, R_2 und R_3 die für Formel I ausgewiesenen Bedeutungen aufweisen,
mit einem Orthoester der Formel XIII



XIII

worin R_4 die für Formel I ausgewiesene Bedeutung aufweist und R_5 C_1-C_5-Alkyl darstellt,
in Gegenwart oder Abwesenheit eines Lösungsmittels, in Gegenwart oder Abwesenheit eines sauren Katalysators, bei 20-200°C, und Gewinnen des Pyrimidin-4-on-derivats der Formel IV; und

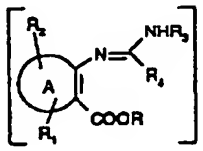
d) falls das Zwischenprodukt VII gebildet wird



VII

Behandeln der Verbindung VII in Gegenwart eines Lösungsmittels und, falls erforderlich, in Gegenwart einer Base, und Gewinnen, unter Ringschluss, des Pyrimidin-4-on-derivats der Formel IV.

16. Verbindung der Formel III



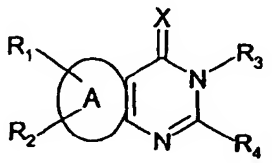
III

worin

A Thienyl[2.3-d] oder Thienyl[3.2-d] darstellt;
R_1 Wasserstoff, Halogen oder Trimethylsilyl darstellt;
R_2 Wasserstoff, Halogen oder Trimethylsilyl darstellt; und mindestens einer der Reste R_1 und R_2 nicht Wasserstoff darstellt;
R_3 C_1-C_8-Alkyl, C_1-C_8-Alkenyl, C_1-C_8-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen, C_1-C_6-Alkoxy oder C_1-C_6-Halogenalkoxy ein- bis dreifach substituiert sind; O-C_1-C_6-Alkyl, O-C_2-C_6-Alkenyl, O-C_2-C_6-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen oder C_1-C_6-Alkoxy ein- bis dreifach substituiert sind; N-C_1-C_6-Alkyl; oder N=CHC_1-C_6-Alkyl darstellt;
R_4 C_1-C_8-Alkyl, C_1-C_8-Alkenyl, C_1-C_8-Alkinyl, die unsubstituiert oder mit C_3-C_6-Cycloalkyl, Halogen, Cyano, C_1-C_6-Alkoxy oder C_1-C_6-Halogenalkoxy ein- bis dreifach substituiert sind; Nitro; -CO-C_1-C_6-Alkyl; C_3-C_6-Cycloalkyl; oder Phenyl, das unsubstituiert oder mit Halogen, C_1-C_6-Alkyl, C_1-C_6-Halogenalkyl, C_1-C_6-Alkoxy, C_1-C_6-Halogenalkoxy, Cyano, Nitro, Amino, Mono-C_1-C_6-alkylamino, Di-C_1-C_6-alkylamino, C_1-C_6-Alkylthio, Phenyl oder Phenoxy ein- bis dreifach substituiert ist, und worin der Phenylteil unsubstituiert oder mit Halogen, C_1-C_6-Alkyl, C_1-C_6-Halogenalkyl, C_1-C_6-Alkoxy oder C_1-C_6-Halogenalkoxy ein- bis dreifach substituiert ist, darstellt; und
R Wasserstoff oder C_1-C_6-Alkyl darstellt.

Revendications

1. Composé de formule I



(I)

dans lequel

A est un thiényle, un thiazolyle, un pyridyle ou un pyridazinyle ;
X est un oxygène ou un soufre ;

R_1 est un hydrogène, un halogène ou un triméthylsilyle ;
R_2 est un hydrogène, un halogène ou un triméthylsilyle ; au moins l'un parmi R_1 et R_2 n'est pas un hydrogène ;
R_3 est un alkyle en C_1 à C_8, un alkényle en C_1 à C_8, un alkynyle en C_1 à C_8 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène, un alkoxy en C_1 à C_6 ou un halogénoalkoxy en C_1 à C_6 ; un O-alkyle en C_1 à C_6, un O-alkényle en C_2 à C_6, un O-alkynyle en C_2 à C_6, qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène ou un alkoxy en C_1 à C_6 ; Un N-alkyle en C_1 à C_6 ; ou un N=CH-alkyle en C_1 à C_6 ;
R_4 est un alkyle en C_1 à C_8, un alkényle en C_1 à C_8, un alkynyle en C_1 à C_8 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène, un cyano, un alkoxy en C_1 à C_6 ou un halogénoalkoxy en C_1 à C_6 ; un nitro ; un -CO-alkyle en C_1 à C_6 ; un cycloalkyle en C_3 à C_6 ; ou un phényle, qui est non substitué ou mono- à tri-substitué avec un halogène, un alkyle en C_1 à C_6, un halogénoalkyle en C_1 à C_6, un alkoxy en C_1 à C_6, un halogénoalkoxy en C_1 à C_6, un cyano, un nitro, un amino, un mono-(alkyle en C_1 à C_6)-amino, un di-(alkyle en C_1 à C_6)-amino, un thioalkyle en C_1 à C_6, un phényle ou un phénoxy et dans lequel la partie phényle est non substituée ou mono- à tri-substituée avec un halogène, un alkyle en C_1 à C_6, un halogénoalkyle en C_1 à C_6, un alkoxy en C_1 à C_6 ou un halogénoalkoxy en C_1 à C_6.

2. Composé de formule I selon la revendication 1, dans lequel
A est un thiényle.

3. Composé de formule I selon la revendication 2, dans lequel

R_1 est un hydrogène, un fluor, un chlore, un brome ou un iode ;
R_2 est un hydrogène, un fluor, un chlore, un brome ou un iode ; au moins l'un parmi R_1 et R_2 n'est pas un hydrogène ;
R_3 est un alkyle en C_1 à C_6, un alkényle en C_2 à C_6, un alkynyle en C_2 à C_6 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène ou un alkoxy en C_1 à C_4 ; un O-alkyle en C_1 à C_6, un O-alkényle en C_2 à C_6, un O-alkynyle en C_2 à C_6, qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène ou un alkoxy en C_1 à C_4 ; un N-alkyle en C_1 à C_6 ; ou un N=CH-alkyle en C_1 à C_6 ;
R_4 est un alkyle en C_1 à C_6, un alkényle en C_2 à C_6, un alkynyle en C_2 à C_6 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène ou un alkoxy en C_1 à C_4 ; ou un phényle qui est non substitué ou mono- à tri-substitué avec un fluor, un chlore, un brome, un alkyle en C_1 à C_4, un halogénoalkyle en C_1 à C_4, un alkoxy en C_1 à C_4, un halogénoalkoxy en C_1 à C_4, un phényle ou un phénoxy et dans lequel la partie phényle est non substituée ou mono- à tri-substituée avec un fluor, un chlore, un brome, un alkyle en C_1 à C_4, un halogénoalkyle en C_1 à C_4, un alkoxy en C_1 à C_4 ou un halogénoalkoxy en C_1 à C_4.

4. Composé de formule I selon la revendication 3, dans lequel

R_3 est un alkyle en C_1 à C_6, un alkényle en C_2 à C_6, un alkynyle en C_2 à C_6 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_4, un fluor, un chlore, un brome ou un alkoxy en C_1 à C_4 ; un O-alkyle en C_1 à C_6, un O-alkényle en C_2 à C_6, un O-alkynyle en C_2 à C_6 ; un N-alkyle en C_1 à C_6 ; ou un N=CH-alkyle en C_1 à C_6 ;
R_4 est un alkyle en C_1 à C_6, un alkényle en C_2 à C_6, un alkynyle en C_2 à C_6 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_4, un fluor, un chlore, un brome ou un alkoxy en C_1 à C_4 ; ou un phényle qui est non substitué ou mono- à tri-substitué avec un fluor, un chlore, un brome, un alkyle en C_1 à C_4, un halogénoalkyle en C_1 à C_4, un alkoxy en C_1 à C_4, un halogénoalkoxy en C_1 à C_4, un phényle ou un phénoxy et dans lequel la partie phényle est non substituée ou mono- à tri-substituée avec un fluor, un chlore ou un brome.

5. Composé de formule I selon la revendication 4, dans lequel

A est un thiényle [2,3-d],
X est un oxygène,
R_1 est un hydrogène, un chlore ou un brome ;
R_2 est un hydrogène, un chlore ou un brome ; au moins l'un parmi R_1 et R_2 n'est pas un hydrogène ;
R_3 est un alkyle en C_3 à C_5 ou un O-alkyle en C_1 à C_4 ;
R_4 est un alkyle en C_2 à C_5 ou un phényle qui est non substitué ou mono- à tri-substitué avec un fluor, un chlore, un brome, un alkyle en C_1 à C_4 ou un phénoxy et dans lequel le phénoxy est non substitué ou mono-

à tri-substitué avec un fluor, un chlore ou un brome.

6. Composé de formule I selon la revendication 4, dans lequel

A est un thiényle [2,3-d],
X est un soufre,
R_1 est un hydrogène, un chlore ou un brome ;
R_2 est un hydrogène, un chlore ou un brome ; au moins l'un parmi R_1 et R_2 n'est pas un hydrogène ;
R_3 est un alkyle en C_3 à C_5 ou un O-alkyle en C_1 à C_4 ;
R_4 est un alkyle en C_2 à C_5 ou un phényle qui est non substitué ou mono- à tri-substitué avec un fluor, un chlore, un brome, un alkyle en C_1 à C_4 ou un phénoxy et dans lequel le phénoxy est non substitué ou mono- à tri-substitué avec un fluor, un chlore ou un brome.

7. Composé de formule I selon la revendication 4, dans lequel

A est un thiényle [3,2-d],
X est un oxygène,
R_1 est un hydrogène, un chlore ou un brome ;
R_2 est un hydrogène, un chlore ou un brome ; au moins l'un parmi R_1 et R_2 n'est pas un hydrogène ;
R_3 est un alkyle en C_3 à C_5 ou un O-alkyle en C_1 à C_4 ;
R_4 est un alkyle en C_2 à C_5 ou un phényle qui est non substitué ou mono- à tri-substitué avec un fluor, un chlore, un brome, un alkyle en C_1 à C_4 ou un phénoxy et dans lequel le phénoxy est non substitué ou mono- à tri-substitué avec un fluor, un chlore ou un brome.

8. Composé de formule I selon la revendication 1, dans lequel
A est un pyridyle.

9. Composé de formule I selon la revendication 1, dans lequel
A est un thiazolyle.

10. Composé de formule I selon la revendication 1, dans lequel
A est un pyridazinyle.

11. Composition pour lutter contre et prévenir l'infestation par des parasites, dans laquelle la substance active est un composé selon la revendication 1 associée à un support adapté.

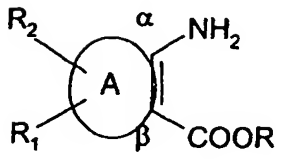
12. Utilisation d'un composé de formule I selon la revendication 1 pour protéger les plantes contre l'infestation par des microorganismes phytopathogènes.

13. Procédé de lutte contre ou de prévention de l'infestation de plantes cultivées par des microorganismes phytopathogènes par application d'un composé de formule I selon la revendication 1 sur des plantes, sur des parties de celles-ci ou sur le site de celles-ci.

14. Procédé selon la revendication 13, dans lequel le microorganisme phytopathogène est un organisme fongique.

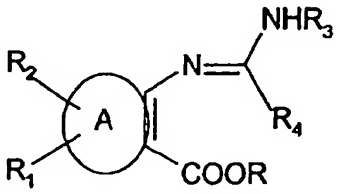
15. Procédé pour la préparation d'un composé de formule I selon la revendication 1, qui comprend les étapes consistant à

a) transformer un α-amino-β-carboalkoxyhétérocycle de formule II, dans lequel R_1 et R_2 sont définis conformément à la formule I et R est un hydrogène, un alkyle en C_1 à C_6,



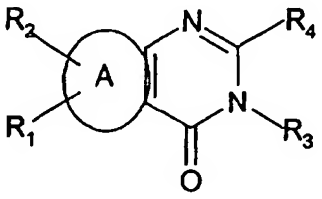
II

avec $POCl_3$ en présence d'un solvant et de R_4CONHR_3 en amidine de formule III, dans laquelle R_3 et R_4 sont définis conformément à la formule I



III ;

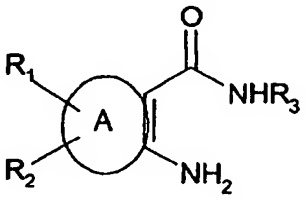
b) et traiter l'amidine, en présence d'un solvant et si nécessaire en présence d'une base, et obtenir, par fermeture du cycle, le dérivé de pyrimidin-4-one de formule IV



IV ;

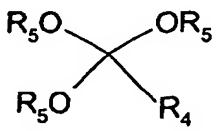
ou

c) faire réagir un amide d'acide aminocarboxylique de formule VI



VI

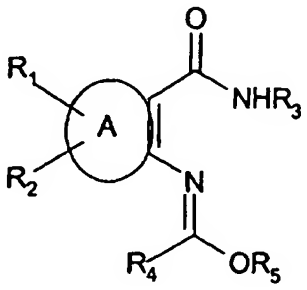
dans lequel A, R_1, R_2 et R_3 sont définis conformément à la formule I
avec un orthoester de formule XIII



XIII

dans lequel R_4 est défini conformément à la formule I et R_5 est un alkyle en C_1 à C_5, en présence ou en l'absence d'un solvant, en présence ou en l'absence d'un catalyseur acide à une température de 20 à

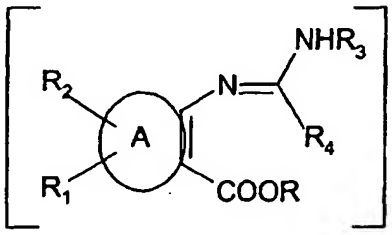
200°C, et obtenir le dérivé de pyrimidin-4-one de formule IV ; et
d) si l'intermédiaire VII est formé



VII

traiter le composé VII en présence d'un solvant et si nécessaire, en présence d'une base et obtenir par fermeture du cycle le dérivé de pyrimidin-4-one de formule IV.

16. Composé de formule III



III

dans lequel

A est un thiényle [2,3-d] ou un thiényle [3,2-d] ;
R_1 est un hydrogène, un halogène ou un triméthylsilyle ;
R_2 est un hydrogène, un halogène ou un triméthylsilyle ; au moins l'un parmi R_1 et R_2 n'est pas un hydrogène ;
R_3 est un alkyle en C_1 à C_8, un alkényle en C_1 à C_8, un alkynyle en C_1 à C_8 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène, un alkoxy en C_1 à C_6 ou un halogénoalkoxy en C_1 à C_6 ; un O-alkyle en C_1 à C_6, un O-alkényle en C_2 à C_6, un O-alkynyle en C_2 à C_6, qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène ou un alkoxy en C_1 à C_6 ; Un N-alkyle en C_1 à C_6 ; ou un N=CH-alkyle en C_1 à C_6 ;
R_4 est un alkyle en C_1 à C_8, un alkényle en C_1 à C_8, un alkynyle en C_1 à C_8 qui sont non substitués ou mono- à tri-substitués avec un cycloalkyle en C_3 à C_6, un halogène, un cyano, un alkoxy en C_1 à C_6 ou un halogénoalkoxy en C_1 à C_6 ; un nitro ; un -CO-alkyle en C_1 à C_6 ; un cycloalkyle en C_3 à C_6 ; ou un phényle, qui est non substitué ou mono- à tri-substitué avec un halogène, un alkyle en C_1 à C_6, un halogénoalkyle en C_1 à C_6, un alkoxy en C_1 à C_6, un halogénoalkoxy en C_1 à C_6, un cyano, un nitro, un amino, un mono-(alkyle en C_1 à C_6)-amino, un di-(alkyle en C_1 à C_6)-amino, un thioalkyle en C_1 à C_6, un phényle ou un phénoxy et dans lequel la partie phényle est non substituée ou mono- à tri-substituée avec un halogène, un alkyle en C_1 à C_6, un halogénoalkyle en C_1 à C_6, un alkoxy en C_1 à C_6 ou un halogénoalkoxy en C_1 à C_6 ; et
R est un hydrogène ou un alkyle en C_1 à C_6.